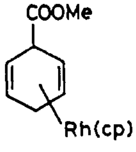
Transition Metal–Diene Complexes. Part 4.[1] The Crystal and Molecular Structure and Isomerization of η-Cyclopentadienyl(η-3-methoxycarbonylcyclohexa-1,4-diene)rhodium(I)

By **Michael G. B. Drew,*** Department of Chemistry, The University, Reading RG6 2AD
Catrionia M. Regan and **S. Martin Nelson,*** Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland

Crystals of the title compound, [Rh(C_5H_6)($C_5H_7CO_2Me$)], are monoclinic, space group *I*2/*a* with cell dimensions *a* = 28.124(14), *b* = 6.141(8), *c* = 14.569(11) Å, β = 112.43(9)°, and *Z* = 8. The intensities of 1 325 reflections above background were collected by counter methods and refined to *R* 0.052. The rhodium atom is bonded to the five carbon atoms of the planar cyclopentadienyl ring [Rh–C 2.197(10)—2.262(13) Å] and to the four olefinic carbon atoms [Rh–C 2.125(13)—2.138(12) Å] of the cyclohexa-1,4-diene. The cyclohexa-1,4-diene ring is in the boat conformation with the two saturated carbon atoms lying 0.66, 0.70 Å above the plane of the four olefinic carbons in a direction away from the metal. The carbomethoxy-subtituent is planar and occupies an axial position with respect to the cyclohexadiene boat. The title complex undergoes a kinetically controlled isomerization when heated in toluene or acid-free *o*-dichlorobenzene to a mixture of complexes containing co-ordinated 5-methoxycarbonyl- (major product) and 2-methoxycarbonyl-cyclohexa-1,3-diene (minor product). In the presence of acid in *o*-dichlorobenzene the major product undergoes a secondary isomerization to the complex containing co-ordinated 1-methoxycarbonylcyclohexa-1,3-diene. For the primary isomerization a mechanism involving the formation of a hydrido-η^3-allylic intermediate is proposed in which the rate-determining step is a carbon-to-metal hydride-ion transfer. For the secondary isomerization, in the presence of acid, a reverse metal-to-carbon hydrogen transfer is believed to operate.

EARLIER papers in this series[1-3] have described the synthesis and characterization of a range of cyclic and acyclic 1,4-dienes co-ordinated to rhodium(I). It was shown[1,3] that when the complexes are heated in non-protic media the co-ordinated 1,4-dienes undergo isomerization to mixtures of (co-ordinated) conjugated dienes. A mechanism involving an η^3-allyl-hydrido-intermediate was proposed in which the rate-determining step is the transfer of a hydrogen from an allylic carbon to the metal. From product distributions observed in the reactions of some methyl substituted cyclohexa-1,4-dienes some evidence was found for the view that the hydrogen is transferred largely as the hydride ion.[1] It was therefore of interest to examine the effect of electron-withdrawing substituents on the isomerization of cyclohexa-1,4-diene complexes.

In the present paper we describe the isomerization of the complex [Rh(cp)(C_6H_7COOMe)] (1) where C_6H_7-COOMe is 3-methoxycarbonylcyclohexa-1,4-diene and cp is the η^5-cyclopentadienyl group. Since no structural information on co-ordinated cyclohexa-1,4-dienes appears to be available, an *X*-ray structure determination of this complex was undertaken. There has been considerable speculation concerning the conformational preferences of uncomplexed cyclohexa-1,4-diene and its derivatives, both planar[4-11] and boat[12-14] conformations having been proposed.



(1)

RESULTS AND DISCUSSION

The title complex was prepared by the displacement of ethylene from di-μ-chloro-tetrakis(ethylene)dirhodium on treatment with 3-methoxycarbonylcyclohexa-1,4-diene followed by treatment with thallium cyclopentadienide. It was characterized by elemental analysis, i.r., mass, and ^1H n.m.r. spectra (see Experimental section), and by the single-crystal *X*-ray structure determination.

Crystal Data.—$C_{13}H_{15}O_2Rh$, $M = 306.0$, Monoclinic, $a = 28.124(14)$, $b = 6.141(8)$, $c = 14.569(11)$ Å, $\beta = 112.43(9)°$, $U = 2\,825.84$ Å^3, $D_m = 1.72$, $Z = 8$, $D_c = 1.75$ g cm^{-3}, $F(000) = 1\,232$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 14.1$ cm^{-1}, space group *I*2/*a* from systematic absences hkl, $h + k + l = 2n + 1$, $h0l$, $h = 2n + 1$, $k = 2n + 1$.

A crystal with dimensions 0.10 × 0.15 × 0.70 mm was mounted with the 100 planes perpendicular to the instrument axis of a General Electrix XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. The apparatus was equipped with a manual goniostat, scintillation counter, and pulse height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with the stationary-crystal-stationary-counter method and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured during the course of the experiment but no significant change in intensity was detected. Of 2 257 independent reflections measured with $2\theta < 50°$, 1 325 with $I > \sigma(I)$ were used in subsequent calculations. No extinction or absorption corrections were applied.

Structure Determination.—The rhodium atom position was determined from the Patterson function and successive Fourier syntheses were used to locate the positions of the remaining atoms. The structure was refined by full-matrix least squares with all atoms except hydrogen given anisotropic thermal parameters. The hydrogen atoms were positioned in accordance with expected geometry; their thermal parameters were refined but not their positional co-ordinates as attempts to do so were unsuccessful. The final R was 0.052. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and (sin θ)/λ was $w^{\frac{1}{2}} = 1$ for $F_o < 160$ and $160/F$ for $F > 160$. The SHEL-X system[15] of computer programs at the University of London Computer Centre was used. Scattering factors were taken from International Tables.[16] In the final cycle of refinement no shift was greater than 0.2 σ. The final difference Fourier showed no significant peaks. The zero-weighted reflections showed no serious discrepancies. Final positional parameters are given in Table 1. Bond distances and angles are in Table 2, and least-square planes in Table 3. Final anisotropic thermal parameters, hydrogen parameters, and observed and calculated structure factors are given in Supplementary Publication No. SUP 23001 (10 pp.).*

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Rh	5 971(0)	2 920(1)	350(1)
C(1)	5 854(5)	479(19)	1 276(8)
C(2)	6 328(5)	127(18)	1 199(8)
C(3)	6 792(4)	1 359(18)	1 891(8)
C(4)	6 573(5)	3 658(19)	1 743(8)
C(5)	6 101(5)	3 988(20)	1 823(8)
C(6)	5 843(4)	2 058(22)	2 081(8)
C(7)	7 016(4)	639(21)	2 969(9)
O(1)	7 147(4)	1 786(15)	3 672(6)
O(2)	7 078(3)	−1 500(13)	3 028(6)
C(9)	7 348(6)	2 401(25)	4 039(10)
C(11)	5 983(5)	2 821(32)	−1 192(8)
C(12)	5 499(5)	2 220(21)	−1 212(6)
C(13)	5 269(6)	4 002(24)	−947(9)
C(14)	5 651(6)	5 659(22)	−681(8)
C(15)	6 070(6)	4 921(27)	− 848(9)

TABLE 2

Molecular dimensions (distances Å; angles °)

Rh–C(1)	2.125(13)	Rh–C(13)	2.251(12)
Rh–C(2)	2.129(11)	Rh–C(14)	2.206(12)
Rh–C(4)	2.137(10)	Rh–C(15)	2.238(16)
Rh–C(5)	2.138(12)		
Rh–C(11)	2.262(13)	Rh–C(6)	2.732(13)
Rh–C(12)	2.197(10)	Rh–C(3)	2.708(9)
C(1)–C(2)	1.40(2)	C(6)–C(1)	1.53(2)
C(2)–C(3)	1.51(1)	C(3)–C(7)	1.52(2)
C(3)–C(4)	1.52(2)	C(7)–O(1)	1.18(2)
C(4)–C(5)	1.39(2)	C(7)–O(2)	1.32(2)
C(5)–C(6)	1.51(2)	O(2)–C(9)	1.48(2)
C(6)–C(1)–C(2)	117.3(10)	C(5)–C(6)–C(1)	98.9(10)
C(1)–C(2)–C(3)	118.4(11)	C(3)–C(7)–O(1)	126.4(11)
C(2)–C(3)–C(4)	99.8(8)	C(3)–C(7)–O(2)	110.4(10)
C(3)–C(4)–C(5)	118.1(11)	O(1)–C(7)–O(2)	123.1(11)
C(4)–C(5)–C(6)	118.1(11)	C(7)–O(2)–C(9)	116.1(9)
C(11)–C(12)	1.40(2)	C(13)–C(14)	1.42(2)
C(11)–C(15)	1.37(2)	C(14)–C(15)	1.37(2)
C(12)–C(13)	1.40(2)		
C(15)–C(11)–C(12)	107.0(14)	C(13)–C(14)–C(15)	109.1(13)
C(11)–C(12)–C(13)	109.7(13)	C(14)–C(15)–C(11)	109.3(14)
C(12)–C(13)–C(14)	104.7(14)		

TABLE 3

Least-squares planes. Distances of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with an asterisk

Plane 1: C(11) −0.02, C(12) 0.03, C(13) −0.03, C(14) 0.02, C(15) 0.00, Rh * 1.89
Plane 2: C(1) −0.00, C(2) 0.00, C(4) −0.00, C(5) 0.00, C(6) * 0.70, C(3) * 0.66, Rh * −1.65
Plane 3: C(3) 0.04, C(7) −0.03, O(1) −0.00, O(2) −0.05, C(9) 0.04

Angles (°) between planes:
1 and 2, 0.9; 2 and 3, 87.4

Discussion of the Structure.—The molecule is shown in Figure 1 together with the atomic numbering scheme. As expected, and as indicated by the n.m.r. spectra (see below), the C_6 and C_5 rings are bonded to the metal in the tetrahapto- and pentahapto-modes, respectively, *i.e.* the metal is bonded to the five cyclopentadienyl carbon atoms [Rh-C 2.197(10)—2.262(13) Å] and to the four olefinic carbon atoms of the cyclohexa-1,4-diene [Rh-C 2.125(13)—2.138(12) Å].

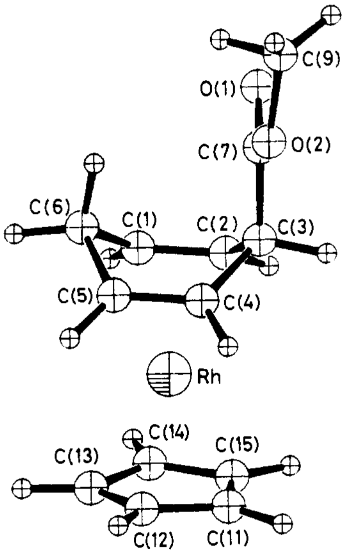


FIGURE 1 The structure of η-cyclopentadienyl(η-3-methoxycarbonylcyclohexa-1,4-diene)rhodium(I) [complex (1)]

The Rh-C and C-C distances in the Rh-cp moiety are in the ranges observed[17-19] in other molecules containing this structural unit. While there are some significant differences among the Rh-C(cp) bond distances (Table 2) there seems to be no correlation of the pattern of variation with respect to the relative position of the substituted diene as is sometimes found.[18] The cp ring is planar (Table 3) and almost parallel to the plane containing the two double bonds of the diene (angle of intersection 0.9°).

The bonds from the metal to the four olefinic carbons of cyclohexa-1,4-diene are equivalent and slightly shorter than those to the cyclopentadienyl moiety. No data for

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

rhodium–1,4-diene complexes are available for comparison but the observed distances in the present molecule are comparable with those found in rhodium(I) complexes with ethylene,[17] 1,3-dienes,[18] and 1,5-dienes.[19,20] The two saturated carbon atoms C(3) and C(6) are bent away by 0.66, 0.70 Å (Table 3) from the metal out of the plane containing the four olefinic carbons, giving the six-membered ring a boat conformation (Figure 1). The Rh • • • C(3) and Rh • • • C(6) distances are 2.708(9) and 2.732(13) Å, and the angles between the planes containing C(2), C(3), C(4), and C(1), C(6), C(5) with the plane of the two double bonds are 44.7 and 42.3°, respectively.

While both planar [4-11] and boat [12-14] conformations for uncomplexed cyclohexa-1,4-diene and its derivatives have been proposed over the past two decades on the basis of spectroscopic and electron diffraction studies, as well as theoretical calculations, the balance of the available evidence is now in favour of a planar conformation. Thus, X-ray diffraction studies of 1-glycylcyclohexa-1,4-diene [9] and *anti*-3,6-dimethoxycarbonyl-1,-2,4,5-tetraphenylcyclohexa-1,4-diene [10] have shown the ring to be planar and the same conclusion has been reached from an ^1H n.m.r. study of 1,4-dihydrobenzyl alcohol in solution.[8] In the latter work it was further concluded that the apparent planarity is not due to rapid boat-to-boat inversion. It appears, then, that the boat conformation adopted by the cyclohexa-1,4-diene ring in the rhodium(I) complex is a direct result of co-ordination. This is a not unexpected result in view of accepted theories of metal–olefin interactions wherein there is a contribution from metallocyclopropane structures leading to some sp^3 character on the olefinic carbon atoms. In this regard it is relevant to note that the C=C double bonds in the rhodium-complexed ring are *ca.* 0.04 Å longer than in uncomplexed 1-glycylcyclohexa-1,4-diene.[9]

The carbomethoxy-substituent occupies an axial position on C(3) of the cyclohexadiene boat. The C(3)–CO_2Me group is planar within 0.04 Å and the angle of intersection of this plane with the C(1), C(2), C(4), C(5) plane is 87.4°. As can clearly be seen from Figure 1 there can be no interaction between the substituent functional groups and the metal atom. There are no intermolecular distances less than the sum of the van der Waals radii in the unit cell.

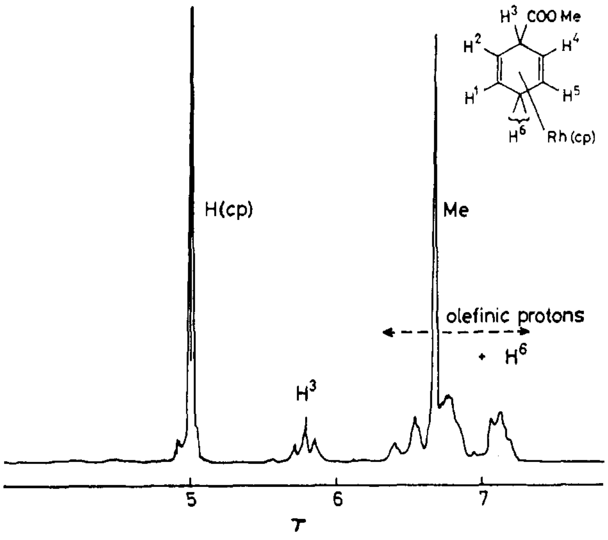


FIGURE 2 ^1H n.m.r. spectrum of (1) in toluene

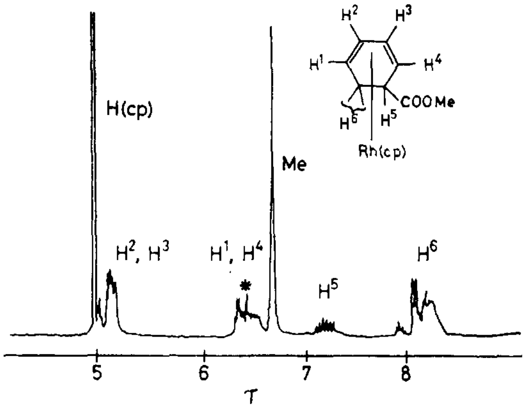


FIGURE 3 ^1H n.m.r. spectrum of the products of isomerization of (1) in toluene. Resonances labelled with an asterisk refer to the minor products

Isomerization of the Co-ordinated Cyclohexa-1,4-*diene*.—The isomerization of the rhodium(I) complex was studied in toluene and in *o*-dichlorobenzene at 70—100 °C by monitoring the ^1H n.m.r. spectra as a function of time. Initially, differences in product distribution and in reaction rate were observed for reactions carried out in the different solvents. It was subsequently found that these variations were largely due to acid impurities in *o*-$C_6H_4Cl_2$.

Reactions in Toluene.—It is first necessary to consider the ^1H n.m.r. spectrum of the reactant (1). This is shown in Figure 2. The cyclopentadienyl protons resonate at τ 4.95, $J_{Rh-H(cp)} = 0.9$ Hz. The proton H(3) is deshielded by the carbomethoxy-group and couples to H(2) and H(4) giving a broad triplet at τ 5.77. The olefinic protons H(1), H(2), H(4), and H(5) and the remaining aliphatic protons H(6) and H(6)′ are extensively coupled forming a multiplet at τ 6.34—7.20. The CH_3 group resonates at τ 6.65. The triplet assigned to H(3) collapsed to a broad singlet when irradiated at τ 6.76 *i.e.* at the midpoint of the H(1), H(2), H(4), H(5) multiplet.

When complex (1) was heated in toluene at 70 °C the ^1H n.m.r. spectrum underwent profound changes. Resonances due to (1) decreased in intensity, apparently in a first-order process, while two new sets of resonances grew steadily until such time as (1) had completely disappeared (*ca.* 6—7 h). The new complexes were formed in the approximate ratio of 94 : 6, this ratio being maintained, as far as could be judged, throughout the reaction. The ^1H n.m.r. spectrum of the completed isomerization mixture is shown in Figure 3. The major product was assigned structure (2) on the basis of the normal (Figure 3) and decoupled spectra (Figure 4). Irradiation at H(6), H(6)′ caused the multiplet at τ 7.15, assigned to H(5), to simplify to a doublet. There was also some simplification in the H(1), H(4) region. Irradiation, at H(5) gave a broad singlet for H(6), H(6)′, with associated changes at H(1), H(4). The most remarkable change was observed on irradiation at H(1), H(4) which caused the multiplet assigned to the central olefinic protons H(2) and H(3) to collapse to a singlet, H(5) to simplify to a triplet, and the H(6), H(6)′ multiplet to simplify to a doublet of doublets. These observations are consistent only with structure (2).

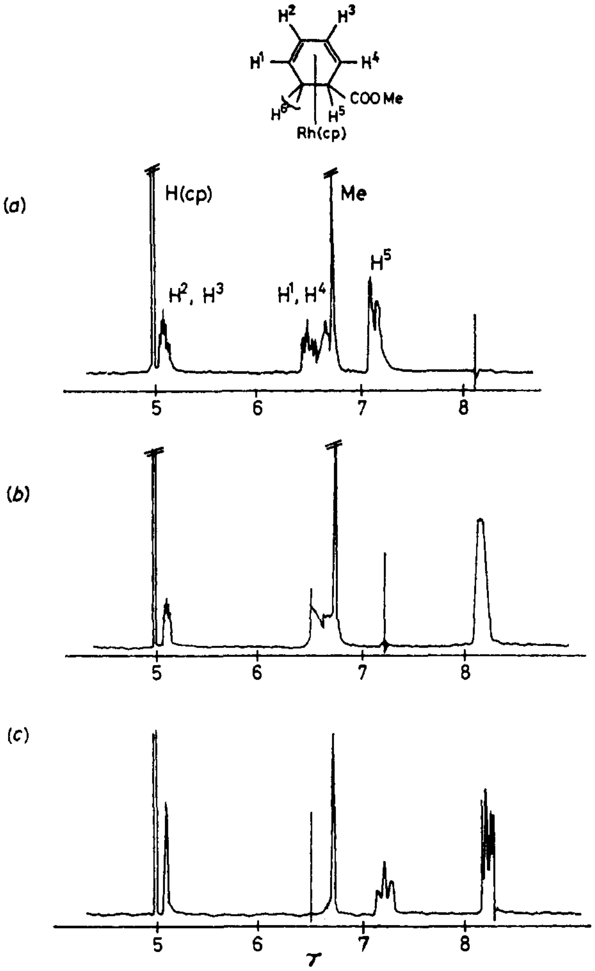
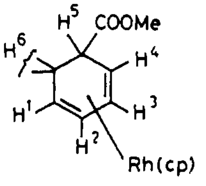
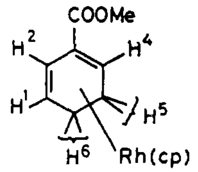


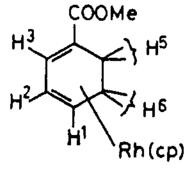
FIGURE 4 Decoupled ^{1}H n.m.r. spectra of (2) in toluene. (a) Irradiated at τ 8.15, (b) irradiated at τ 7.15, (c) irradiated at τ 6.65



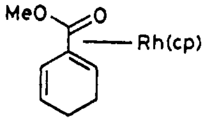
(2)



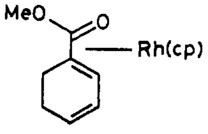
(3)



(4)



(5)



(6)

The assignment of structure to the minor product of the isomerization carried out in toluene proved more difficult. Because of the occurrence of this isomer in a mixture containing a *ca.* 20-fold more abundant isomer (2), decoupling experiments could not be usefully applied. There are five possible isomeric complexes derived from (1) containing a conjugated disposition of double bonds within the cyclohexadiene ring. Two of these, (5) and (6), are heterodiene–rhodium complexes, and can reasonably be excluded on the basis of the following considerations. Firstly, while several iron(0)–heterodiene complexes are known,[21] no corresponding rhodium(I) complexes of this class have yet been reported. It is noteworthy that dibenzylideneacetone co-ordinates to Rh^I as a homo-1,4-diene in preference to the hetero-1,3-diene alternative.[22] In the present work attempts to prepare heterodiene rhodium(I) complexes were made by treating acrylaldehyde, methacrylaldehyde, and cinnamaldehyde with [{RhCl(C$_2$H$_4$)$_2$}$_2$], but without success. Bearing in mind that (5) and (6) might be expected to have different ^{1}H n.m.r. spectra from that found for the minor product (*e.g.* the unco-ordinated olefinic protons would be expected to resonate at lower field) we can rule out (5) and (6) as reaction products. Similarly, the non-conjugated diene complex wherein the carbomethoxy-substituent is attached to an olefinic carbon can be discounted on the basis of the n.m.r. data. Since (2) is already accounted for as the major product, the minor product must be either (3) or (4). The problem was answered by the preparation of a third (different) isomeric complex shown to have structure (4) by carrying out the isomerization in *o*-C$_6$H$_4$Cl$_2$, as described below.

Reactions in o-*Dichlorobenzene*.—When complex (1) was heated in unpurified *o*-C$_6$H$_4$Cl$_2$ at 70 °C for 7 h the ^{1}H n.m.r. spectrum revealed that all (1) had reacted to give two products in an 80 : 20 ratio. Addition of hexane to the product mixture led to crystallization of the two components, the major one as dark green crystals, the minor one as yellow crystals. It was possible to isolate the major product by hand separation of the crystals. Tabulated ^{1}H n.m.r. data for this complex are in Table 4 and the normal and decoupled spectra are shown in Figure 5. It is expected that irradiation in the region of the aliphatic protons would simplify both resonances (iii) and (iv) (see Table 4) if the complex is (3), but that only resonance (iv) would be simplified if the complex is (4). In fact, irradiation at τ 8.3 simplified (to a doublet) resonance (iv) only (Figure 4). Again, irradiation at resonance (iii) at τ 5.3 would have little effect on signals (i) and (iv) if the complex is (3). On the other hand, if the complex is (4), then simplification of both resonances (i) and (iv) should occur. The Figure shows, in fact, that the irradiation produced a collapse

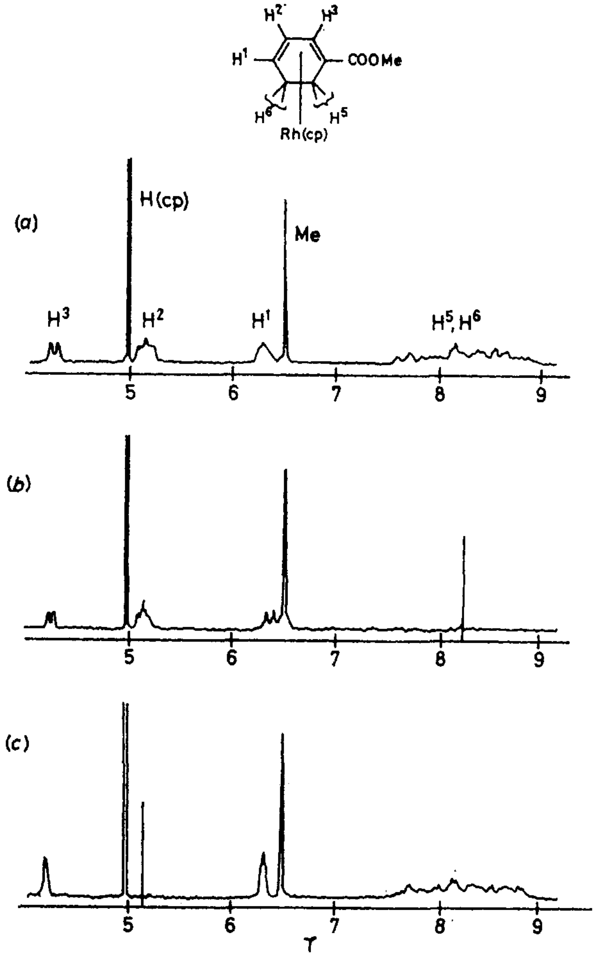


FIGURE 5 Normal and decoupled ^1H n.m.r. spectra of (4) in undistilled *o*-dichlorobenzene. (*a*) Normal spectrum, (*b*) irradiated at τ 8.3, (*c*) irradiated at τ 5.3

of the doublet (i) to a singlet and of the multiplet (iv) to a much simpler pattern. The dark green complex therefore has structure (4).

The yellow minor reaction product in *o*-$C_6H_4Cl_2$ was not obtained in a pure form and since it has a very similar n.m.r. spectrum to that of complex (4) it was not possible to obtain a clean-cut spectrum of this isomer. However, the sharp singlet due to the CH_3 group occurs τ 0.2 to lower field than that in (4). Since in methyl-substituted cyclohexa-1,3-diene complexes of rhodium(I) a methyl group on an inner olefinic carbon resonates at *ca.* τ 0.35 lower field than on a terminal olefinic carbon,[1] a similar, though smaller, chemical-shift difference might be expected for analogous carbomethoxy-substituted cyclohexa-1,3-diene complexes. We therefore assign the minor product (*o*-$C_6H_4Cl_2$ reaction) to complex (3), the only structure which has not been assigned or rejected.

TABLE 4

Hydrogen-1 n.m.r. data for the green (major) product of isomerization of (1) in undistilled *o*-dichlorobenzene

Resonance	Position (τ)	Relative intensity	Multiplicity *	Assignment If complex (3)	Assignment If complex (4)
(i)	4.3	1	d	H^2	H^3
(ii)	4.98	5	d	H (cp)	H (cp)
(iii)	5.3	1	m	H^4	H^2
(iv)	6.4	1	m	H^1	H^1
(v)	6.58	3	s	CH_3	CH_3
(vi)	7.6—9.0	4	m	H^5, H^6	H^5, H^6

* s = Singlet, d = doublet, m = multiplet.

The CH_3 resonance of the minor product of the isomerization in toluene coincides with that identified above as due to complex (3). The products of isomerization in toluene are therefore (2) and (3).

The isomerization of (1) in unpurified *o*-$C_6H_4Cl_2$ was investigated more fully. Nuclear magnetic resonance monitoring throughout the course of the reaction at 70 °C revealed a more complex reaction. As shown in Figure 6 two products are formed initially, at different rates, as the reactant decays but one isomerizes further giving only two products (3) and (4), in the ratio 20 : 80 in the spectrum of the completed reaction mixture. The complex which was initially formed at the faster rate and whose concentration passed through a maximum at *ca.* 2 h (70 °C) was identified as (2) by comparison of its n.m.r. spectrum with that of the major reaction product in toluene. Thus, the primary isomerization in *o*-$C_6H_4Cl_2$ is qualitatively the same as that in toluene in generating (2) as the major and (3) as the minor product. The possibility that the secondary isomerization (2) to (4) [and possibly, also, (3) to (4)] which occurs in *o*-$C_6H_4Cl_2$ might be due to acid impurity in this solvent was tested. Firstly, the isomerization was carried out in triply distilled *o*-$C_6H_4Cl_2$. At 100 °C only *ca.* 10% conversion of (2) to (4) occurred after 7 h; this compares with 100% conversion in *ca.* 1 h in undistilled *o*-$C_6H_4Cl_2$ at the same temperature. In a second test an *o*-$C_6H_4Cl_2$ solution of (2) [generated from (1) in toluene] was treated with HCl gas for a few seconds prior to recording the n.m.r. spectrum at ambient temperature. This showed that the secondary isomerization was complete, only (3) and (4) being observed, in *ca.* 5 : 95 ratio.

Mechanisms of the Isomerizations.—The results described show that the co-ordinated cyclohexa-1,4-

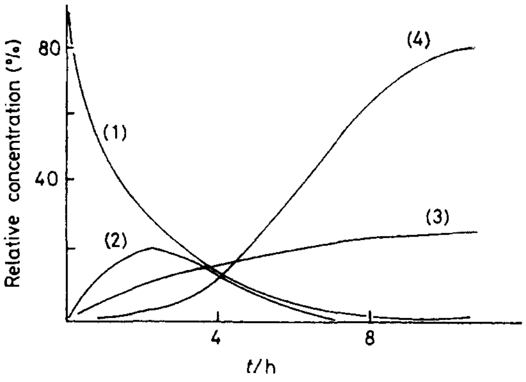
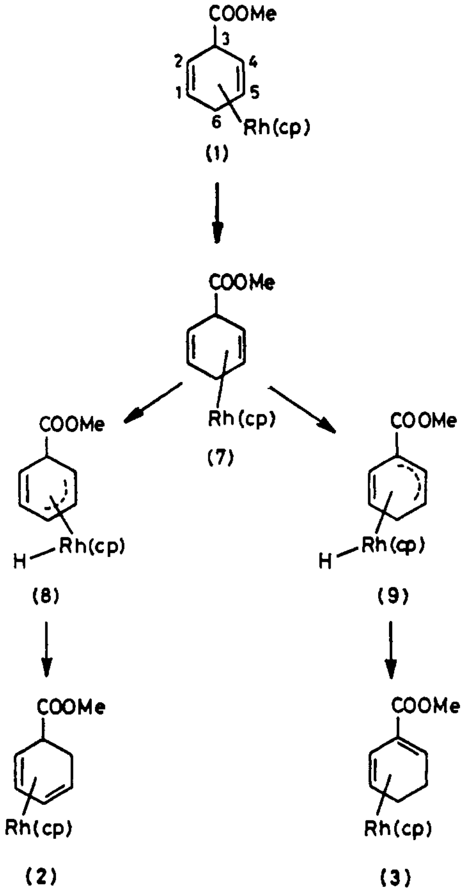


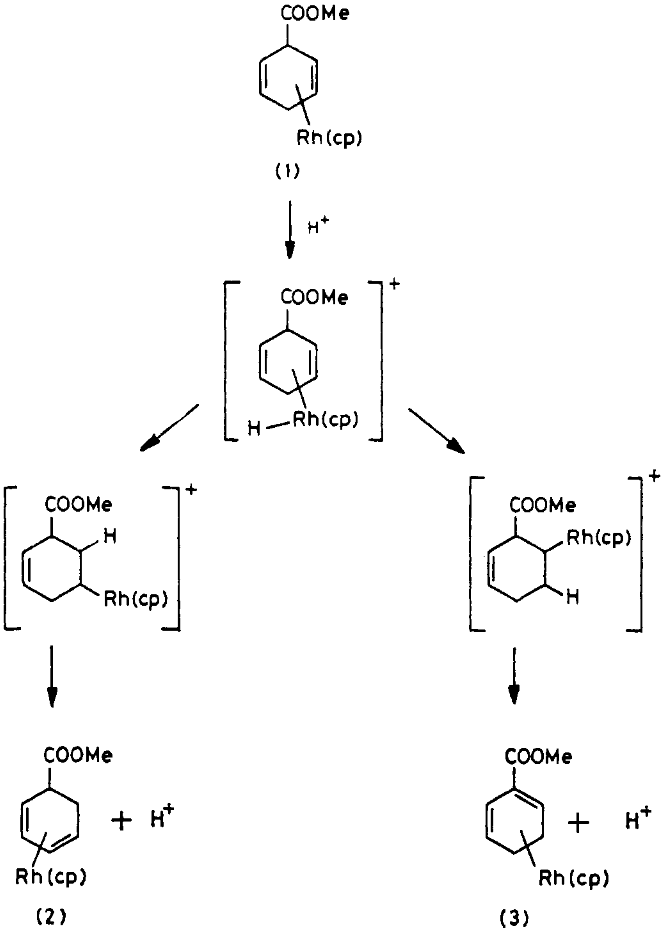
FIGURE 6 Isomerization of (1) in undistilled *o*-dichlorobenzene at 70 °C

diene isomerizes to a mixture of two cyclohexa-1,3-dienes (2) and (3), when heated in aprotic solvents, complex (2), in which the carbomethoxy-substituent is attached to a saturated carbon atom, being the major product. When an external proton source is present a more rapid secondary isomerization which converts (2) to (4) occurs to give a mixture of complexes (3) and (4) in a ratio which presumably reflects the thermodynamic stability ratio of the two complexes. The primary and secondary isomerizations clearly occur *via* different mechanisms.

Considering the primary isomerization first we can apply the mechanism described in Part 3[1] which successfully accounted for the isomerization of a number of co-ordinated methyl-substituted acyclic and cyclic 1,4-dienes to mixtures of conjugated products. In this mechanism (see Scheme 1) the first step is seen as a dissociation of one of the two double bonds from the metal to yield the ' 16-electron ' species (7). This is followed by a carbon-to-metal hydrogen transfer, considered to be the rate-determining step, to form a hydrido-η^3-allylic intermediate. Since two C-to-Rh hydrogen transfers, C(6)-to-Rh and C(3)-to-Rh, are possible, two η^3-allyls (8) and (9) can be formed according to the relative magnitudes of the activation energies controlling the two hydrogen-transfer steps. Since the product analysis has shown complex (2) to be the major product we may conclude that the hydrogen transfer from the unsubstituted carbon C(6) is the preferred path. Now, since the carbomethoxy-group is strongly electron withdrawing in its electronic influence, the hydrogen on C(3) is expected to be more acidic than those on C(6). The implication is that the hydrogen is transferred largely as the hydride anion, in agreement with more tentative conclusions reached earlier from studies on methyl-substituted systems.[1] A radical mechanism cannot be excluded, however.



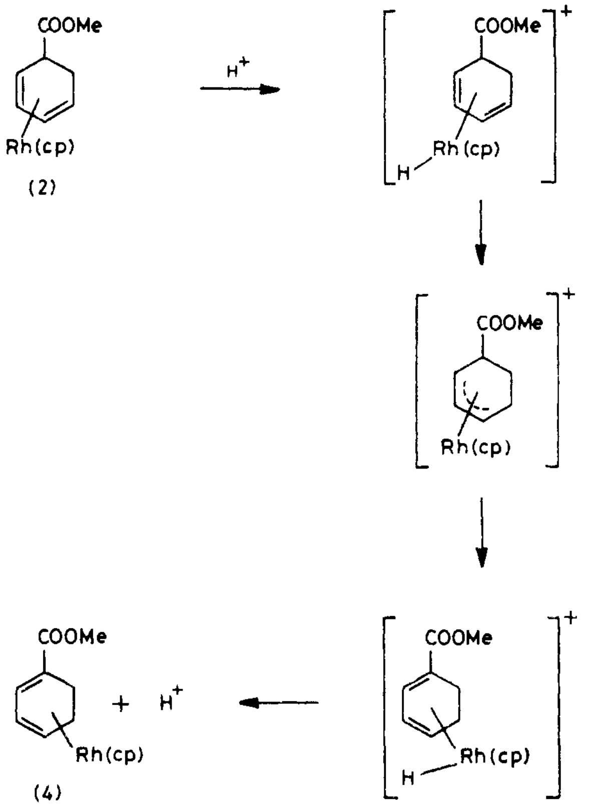
SCHEME 1



SCHEME 2

In the presence of acid the metal hydride addition–elimination mechanism[23] (Scheme 2) may be expected to compete to an extent dependent on the acid concentration.

While Scheme 1 cannot provide a pathway for the secondary isomerization (2) to (4), this conversion can be accounted for, in the presence of acid, by the mechanism of Johnson *et al.*[24] summarised in Scheme 3. The reason that complex (4) is the thermodynamically most stable product is presumably related to the linear conjugation contained in this structure. It is clear that the primary isomerization, carried out under acid-free conditions, is under kinetic control.



SCHEME 3

EXPERIMENTAL

3-Methoxycarbonylcyclohexa-1,4-*diene*.—This was prepared by Birch reduction of benzoic acid followed by esterification. Benzoic acid (10 g, 0.082 mol) was added to anhydrous EtOH (100 cm^3) in a 2-l three-necked flask. Liquid NH_3 (600 cm^3) was condensed into the flask and sodium (6.2 g, 0.27 mol) was added in small pieces over 1 h. When the blue colour had disappeared and all the sodium had been consumed $[NH_4]Cl$ (14.6 g, 0.27 mol) was added cautiously. The mixture was stirred for 1 h and allowed to stand until the NH_3 had evaporated. The residue was dissolved in H_2O (300 cm^3), poured into ice (200 g), and acidified to pH 4 by addition of 10% HCl solution. The resulting mixture was extracted (4 × 100 cm^3) with peroxide-free diethyl ether and the combined extracts washed with aqueous NaCl and dried over $Mg[SO_4]$. The residual oil, obtained on concentration, was distilled (80—98 °C at 0.01 mmHg *) to give dihydrobenzoic acid (7.0 g, 68%) as a colourless oil.

Concentrated H_2SO_4 (2 cm^3) was added to dihydrobenzoic acid (7 g, 0.057 mol) in MeOH (20 cm^3) and the mixture refluxed for 1 h, then cooled and poured into H_2O (50 cm^3). The ester was extracted with Et_2O, washed with H_2O and then 5% $Na[HCO_3]$ followed by aqueous NaCl, and dried over $Mg[SO_4]$. Solvent was removed and the residue distilled to yield 3-methoxycarbonylcyclohexa-1,4-diene.

η-Cyclopentadienyl(*η*-3-*methoxycarbonylcyclohexa*-1,4-*diene*)*rhodium*(I).—Excess of diene was added to a suspension of di-μ-chloro-tetrakis(ethylene)dirhodium(I) in dry degassed Et_2O and gently refluxed for 2 h. The supernatant liquid was decanted and the yellow-orange solid dried *in vacuo*. This was stirred with a slight excess of thallium cyclopentadienide in light petroleum at 20 °C for 3 h. Filtration followed by concentration gave yellow crystals of product after 1 h (Found: C, 51.2; H, 4.8. $C_{13}H_{15}O_2Rh$ requires C, 51.0; H, 4.9%). The complex was characterized by i.r., mass ($P^+ = 306$, $M = 306$), and ^1H n.m.r. spectra (see above).

The isomerization reactions were monitored as described previously.[3]

We thank the Department of Education, N. Ireland, for a postgraduate research award (to C. M. R.).

[0/1317 *Received*, 21*st August*, 1980]

REFERENCES

[1] Part 3, M. Arthurs, C. M. Regan, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 2053.

[2] S. M. Nelson, M. Sloan, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1973, 2195.

[3] M. Arthurs, M. Sloan, M. G. B. Drew, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1975, 1794.

[4] H. D. Stidham, *Spectrochim. Acta*, 1965, **21**, 23.

[5] B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, 1964, **12**, 129.

[6] E. W. Garbisch and M. G. Griffith, *J. Am. Chem. Soc.*, 1958, **90**, 3590.

[7] G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1967, **1**, 117.

[8] J. W. Paschal and P. W. Rabideau, *J. Am. Chem. Soc.*, 1974, **96**, 272.

[9] R. J. Jandacek and S. H. Simonsen, *J. Am. Chem. Soc.*, 1969, **91**, 6663.

[10] M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *J. Am. Chem. Soc.*, 1971, **93**, 4063.

[11] N. L. Alliner and J. T. Sprague, *J. Am. Chem. Soc.*, 1972, **94**, 5734.

[12] H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, 1969, **91**, 10.

[13] L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 1965, 455; D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 1969, 2335.

[14] J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, 1970, **35**, 2038; J. L. Marshall and T. K. Folsom, *ibid.*, 1971, **36**, 2011; but see also, J. L. Marshall, A. M. Ohrig, and P. N. Jenkins, *ibid.*, 1972, **37**, 1863.

[15] G. M. Sheldrick, SHEL-X '76, personal communication.

[16] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[17] L. J. Guggenberger and R. Cramer, *J. Am. Chem. Soc.*, 1972, **94**, 3779.

[18] M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Organomet. Chem.*, 1972, **39**, C9.

[19] M. Arthurs, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1977, 779.

[20] J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*,1970, **26**, 985; P. A. Tucker, W. Scutcher, and D. R. Russell, *ibid.*, 1975 **31**, 592.

[21] A. M. Brodie, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1972, 2031; A. Vessieres and P. Dixneuf, *J. Organomet. Chem.*, 1976, **108**, C5; A. de Cian and R. Weiss, *Chem. Commun.*, 1968, 348.

[22] H. B. Lee and P. M. Maitlis, *J. Organomet. Chem.*, 1973, **57**, C87.

[23] See, for example, C. A. Tolman in 'Transition Metal Hydrides,' ed. E. L. Meutterties, Marcel Dekker Inc., New York, 1972, p. 271.

[24] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1974, 1054.

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.