Site-specific and Random Degenerate Rearrangements in η^6- and η^4-Cycloheptatriene Metal Complexes

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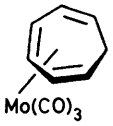
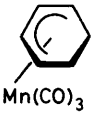
Carbon-13- labelled cycloheptatriene, containing ^{13}C at the 3- and 7-positions, was synthesised from [^{13}C-*carboxy*]-1,4-dihydrobenzoic acid by successive lithium aluminium hydride reduction, toluene-*p*-sulphonylation, and solvolysis in acetic acid. This was converted into the corresponding tricarbonylmolybdenum complex, which was subjected to thermolysis in [$^2H_6$]benzene solution. The course of reaction was followed by ^{13}C n.m.r. spectroscopy, and the redistribution of isotopic label in the product compared with that predicted from solving the differential equations describing the kinetics for each of the possible rearrangement pathways. It was thus shown that a [1,5] hydride shift is involved, in keeping with earlier conclusions of Pauson but not with the observations of Grimme and Roth, or those of Faller. Isotopically enriched cycloheptatrienerhodium(I) acetylacetonate was prepared similarly, and its thermal degenerate rearrangement shown to occur with random redistribution of the label.

One of the characteristic reaction pathways of metal π-olefin complexes is the reversible transfer of an α-hydrogen atom to the metal. This can lead to the isomerisation of acyclic species [1] and to isomerisation or degenerate rearrangement in the complexes of cyclic olefins.[2] This latter case is exemplified by cycloheptatriene, which itself undergoes a [1,5] hydride shift at 140 °C, revealed by deuterium labelling.[3] Its η^6-tricarbonylmolybdenum complex containing a single stereochemically random deuterium atom at the 7-position was shown to undergo an intramolecular rearrangement [4] in which the *endo*-proton of (1) was transferred to the metal and then returned to a different site in the ring, leading to an apparent isomerisation of the *exo*-deuterium atom. It was claimed that this reaction was unselective so that



(1)



(2)

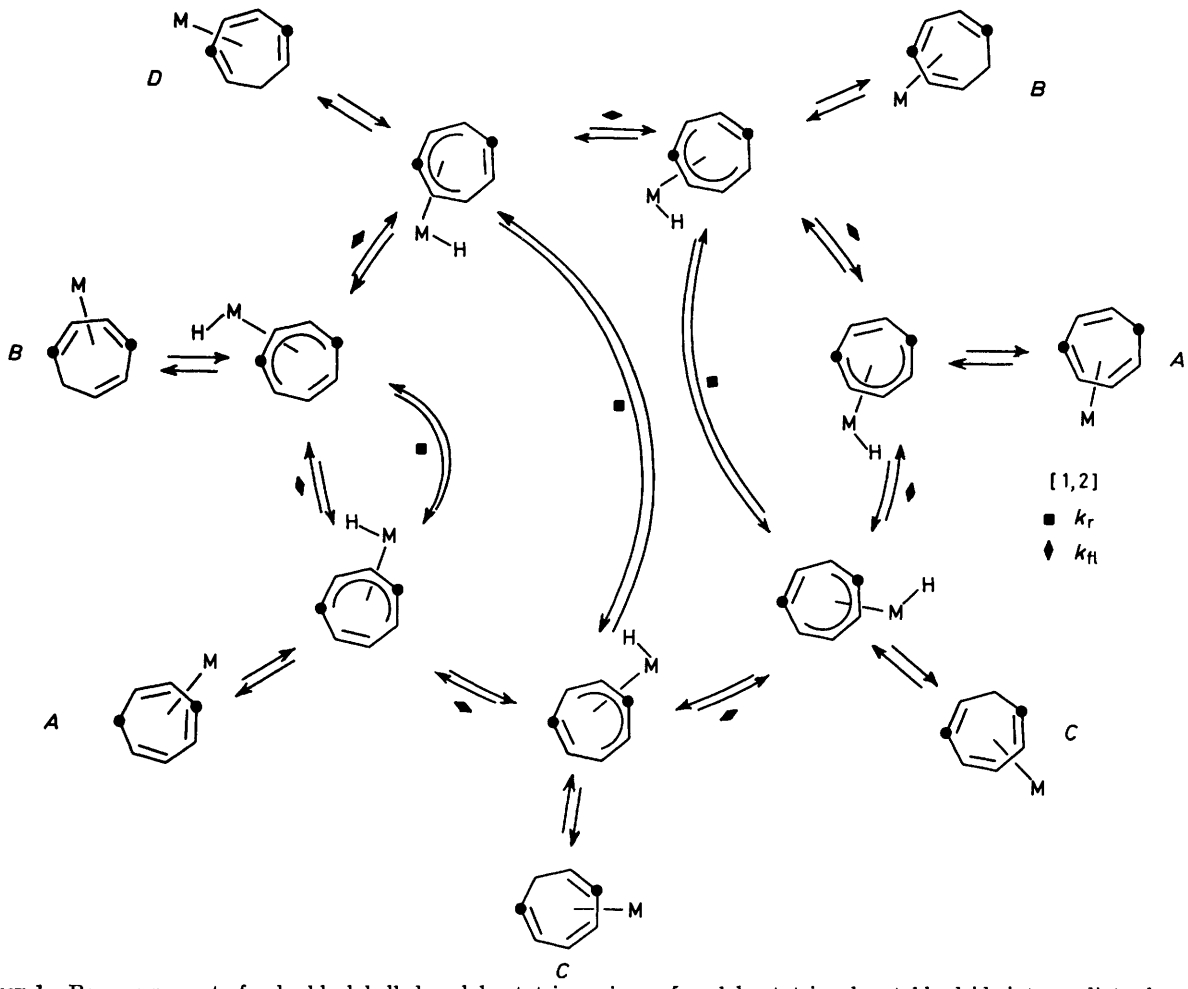
rearrangement distributed the deuterium randomly over the possible ring sites. This contrasts with the observation of Pauson and his co-workers,[5] who showed that η^7-tropyliumtricarbonylchromium cations were attacked by nucleophiles from the *exo*-direction, permitting the preparation of η^6-*exo*-7-alkyl- and 7-aryl-cycloheptatrienetricarbonyl complexes. It was demonstrated that these rearrange by a specific *endo*-[1,5] hydride migration, and the corresponding 7-*endo*-alkylcycloheptatriene complexes † are thermally inert under the reaction conditions. Support for the initial contention of Roth and Grimme is maintained in a recent communication by Faller [2a] who repeated their experiment but monitored the product by the much more sensitive technique of ^2H n.m.r. spectroscopy. He additionally showed that a considerable portion of the reaction between η^7-tropyliumtricarbonylmolybdenum and sodium [$^2H_4$]borohydride occurs from the *endo*-direction, to give a 28 : 72 mixture of *endo*- and *exo*-7-deuteriated cycloheptatriene complexes. This leads to a suggestion, in accord with the conclusions of Lammana and Brookhart based on the thermal isomerisation of (2),[2b] that degenerate hydrogen-atom transfers in cyclopolyene and cyclopolyenyl metal complexes are random processes. The results of Pauson's work, where a preference for [1,5] migration is very clear, are then due to perturbation by the 7-substituent.

Any rearrangement involving the migration of 7-*endo*-hydrogen is likely to require the formation of a tropylium metal hydride at low concentration. To maintain an 18-electron configuration, this must be an η^5-pentadienyl complex (Scheme 1) with an uncomplexed double bond. Similar η^5-tropylium complexes undergo rapid degenerate rearrangement.[6] The specificity of isomerisation then depends on the relative rates of hydride return k_r and of fluxional process k_{fl}. Given the specificity observed by Pauson and his co-workers in an unambiguous case [5] and the dangers inherent in the design of other experiments quoted, we felt it desirable to examine the degenerate rearrangement of cycloheptatriene metal complexes using a ^{13}C-enriched reactant to define the reaction pathway.

Synthesis of ^{13}C-*Labelled Cycloheptatriene*.—Our preparative route is outlined in Scheme 2. A standard solution of phenylmagnesium bromide in ether (0.40M) was treated with gaseous carbon dioxide (from $BaCO_3$, 19% enriched in ^{13}C, and H_2SO_4) at −25 °C.[7] The resulting enriched benzoic acid (3) was reduced by sodium in liquid ammonia to 1,4-dihydrobenzoic acid (4), in turn reduced by lithium aluminium hydride to 1,4-dihydrobenzyl alcohol (5). This was converted into the corresponding toluene-*p*-sulphonate (6) by toluene-*p*-sulphonyl chloride in pyridine, as previously described for the unlabelled compound.[8] Examination of the ^{13}C spectra of the series in $CDCl_3$ confirmed isotopic integrity and additionally demonstrated a progressive diminution in the one-bond coupling constant $J_{1,7}$ from 54 in (4) to 44 in (5) and 38 Hz in (6).[9]

Solvolysis of the unlabelled analogue of (6) at 90 °C has

† This is certainly the case in the corresponding chromium complexes, *cf.* ref. 5.



SCHEME 1 Rearrangement of a doubly labelled cycloheptatriene *via* an η^5-cycloheptatrienyl metal hydride intermediate showing the competition between hydride return and ring fluxionality

been reported to give cycloheptatriene as the major hydrocarbon product.[8] Following a series of trial experiments which optimised the yield on a small scale, the enriched tosylate (6) was heated in acetic acid (0.4M in NaH_2PO_4) at 93 °C for 6 h with continuous removal of volatile products. Work-up as described in the Experimental section gave enriched cycloheptatriene (7) contaminated by 6% toluene, which was examined by ^{13}C n.m.r. (CD_2Cl_2). This demonstrated that isotopic enrichment was distributed in 52 : 48 ratio between C-3 and -7, consistent with the formation of a delocalised carbonium ion along the major product-determining pathway. Intermediates of related structure have already been proposed in the solvolysis of a variety of $(CH)_5(CH_2)_2OR$ compounds.[10] This enriched cycloheptatriene proved to be very suitable for the study of thermal rearrangements, as will be demonstrated.

Preparation and Thermolysis of Complexes of (7).— Enriched cycloheptatriene was converted into its η^6-tricarbonylmolybdenum complex (8) by reaction with trisacetonitriletricarbonylmolybdenum [11] in hexane solution, and the red crystalline product purified by sublimation (70 °C, 0.05 mmHg). A ^{13}C n.m.r. spectrum of the product showed that no rearrangement of the isotopic label had occurred during the synthesis of the complex, but that earlier shift assignments of C-2 and -3 need to be reversed.[12] Spin–lattice relaxation times were determined for the four cycloheptatriene carbon nuclei of the unlabelled complex by a conventional (180°–τ–90°–T) sequence of pulses. The results (Table 1) demonstrate

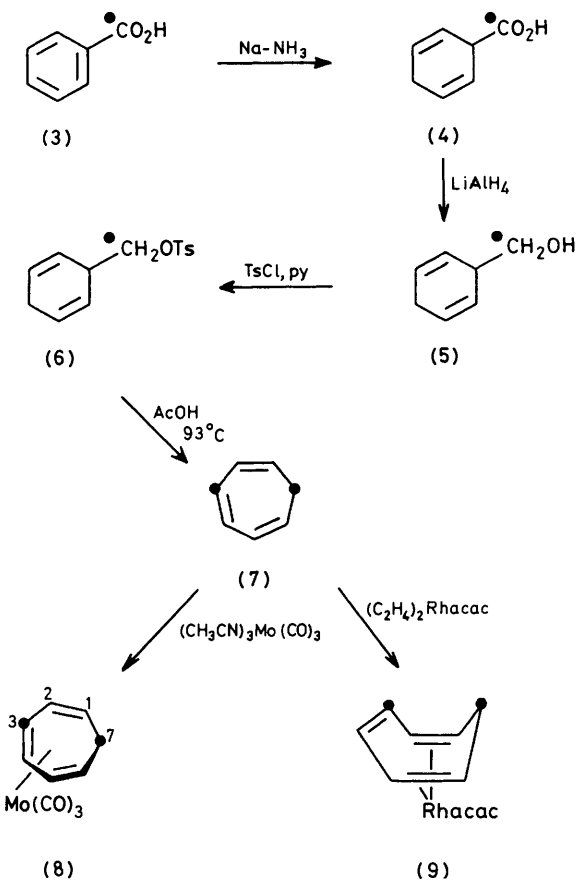
TABLE 1

Spin–lattice relaxation times of ^{13}C nuclei in cycloheptatrienetricarbonylmolybdenum in [$^2H_6$]benzene

Nucleus	C-1	C-2	C-3	C7
T_1/s	4.74 ± 0.15	4.57 ± 0.17	4.30 ± 0.16	2.33 ± 0.23

that NT is very similar at all four sites, showing that the main dipole–dipole relaxation is engendered by overall rather than internal molecular motion.[13] Accurate intensities are only obtained when the delay between 90° pulses is $\geqslant 5T_1$ for the slowest relaxation and in this case an interval of over 20 s would be required. For practical purposes a delay of 3.5 s was used (90° pulse angle), the intensity of C-7 then being multiplied by 0.68 for normalisation purposes.*

* $(1 - e^{\tau/T_{1(C\text{-}2)}})/(1 - e^{\tau/T_{1(C\text{-}7)}}) = 0.68$ when $\tau = 3.5$ s.



SCHEME 2 Synthetic route to ^{13}C-labelled cycloheptatriene and its molybdenum and rhodium complexes

Thermolysis of samples of (8) was carried out in [$^2H_6$]benzene solution at 95—100 °C in tubes sealed under nitrogen. Two batches of complex (8) were utilised, one containing 16% of ^{13}C enrichment and the other 19% of ^{13}C enrichment, based on ^{13}C n.m.r. analysis. Samples were filtered under nitrogen into 10 mm n.m.r. tubes and the ^{13}C spectra recorded. The relevant portion of the transformed spectrum was plotted on a sweep width of 5 Hz cm^{-1} and peak areas determined by standard triangulation procedures. Area analysis employing a Dupont curve resolver gave essentially identical results. Results obtained are recorded in Table 2.

TABLE 2

Corrected percentage enrichment at the cycloheptatriene carbon nuclei in (8). In sample A, the overall enrichment was 16% and in sample B the overall enrichment was 19%. Sample A was thermolysed at 95 ± 1 °C and sample B at 100 ± 1 °C in [$^2H_6$]benzene

Time/min	Sample	C-1, -6	C-2, -5	C-3, -4	C-7
0	A			53	47
150	A	11	3	52	34
210	A	11	3	57	29
0	B			51	49
140	B	8	2.5	54	35.5
255	B	17.5	4.5	48	30
345	B	23.5	5.5	48.5	22.5

It is apparent that the major change on rearrangement is depletion of C-7 and concomitant selective enrichment of C-2. This supports, but does not prove, the involvement of a [1,5] hydrogen shift, since a random mechanism would enrich C-1 and -2 equally whilst a [1,3] shift would enrich C-2 faster than C-1. The main problem is in distinction from a selective [1,2] shift (Scheme 1) which gives rise to rather similar qualitative changes. For this reason a formal mathematical analysis was undertaken which demonstrates the preference for a [1,5] shift mechanism quite unequivocally.

The preparation of η^4-(1—2, 5—6)cycloheptatriene-rhodium(I) acetylacetonate has been reported previously and the rearrangement of its [7-^2H] analogue observed although the experiment did not permit a distinction between different shift mechanisms.[14] For this reason the enriched complex (9) was prepared from ^{13}C-labelled cycloheptatriene and bis(ethylene)rhodium(I) acetylacetonate, and samples thermolysed in [$^2H_6$]benzene solution at 61 °C, with monitoring by ^{13}C n.m.r. and analysis as described above. In this case loss of signal intensity at C-7 and -3 was associated with a concomitant and equal increase in the intensities of C-1 and -2 over more than one half-life. This is consistent only with the random mechanism of rearrangement.

Analysis of Seven-site Scrambling.—In this section we solve the differential equations to describe the position of ^{13}C in the seven different positions of the ring as a function of time. At the start of the thermolysis the ^{13}C is at positions 7, 3, and 4 in the proportions 2, 1, and 1 respectively. By the end of the thermolysis the ^{13}C is randomly distributed with 14.3% on each of the seven sites. We consider each of the following mechanisms in turn, [1,2], [1,3], and [1,5] shifts and random scrambling. It is convenient to define for each site the dimensionless concentration u_n which is defined by equation (1). We

$$u_n = \frac{[^{13}C \text{ on site } n]}{\Sigma[^{13}C]} \quad (1)$$

assume that for a particular mechanism the same rate constant k controls the exchange of isotope and we define the dimensionless time τ by equation (2). The boundary

$$\tau = kt \quad (2)$$

conditions at $\tau = 0$ are $u_7 = \frac{1}{2}$, $u_3 = u_4 = \frac{1}{4}$, and $u_1 = u_2 = u_5 = u_6 = 0$. From the symmetry of these conditions and of the molecule it is clear that throughout, $u_1 = u_6$, $u_2 = u_5$, and $u_3 = u_4$. Hence for each mechanism we have to find how u_1, u_2, u_3, and u_7 vary with τ. We do this by writing down normal kinetic equations and converting to the dimensionless variables. For instance for site 7 with a [1,2] shift (as shown above) equation (3) applies. We then take the Laplace transform of the

$$du_7/d\tau = u_1 + u_6 - 2u_7 = 2u_1 - 2u_7 \quad (3)$$

four equations for each mechanism to obtain for instance for equation (3), $s\bar{u}_7 - \frac{1}{2} = 2\bar{u}_1 - 2\bar{u}_7$. Solution of the set of four simultaneous equations for each of the shift

mechanisms then gives equations (4)—(7) where the

$$\bar{u}_1 = (a_1s^2 + b_1s + c_1)/4sD \quad (4)$$

$$\bar{u}_2 = (a_2s^2 + b_2s + c_2)/4sD \quad (5)$$

$$\bar{u}_3 = \tfrac{1}{4}s - (a_3s^2 + b_3s + c_3)/4sD \quad (6)$$

$$\bar{u}_7 = \tfrac{1}{2}s - (a_7s^2 + b_7s + c_7)/4sD \quad (7)$$

coefficients a_n, b_n, and c_n are given in Table 3. The denominator D for each shift mechanism is given by equation (8). The form of equations (4)—(7) together

$$D = s^3 + 7s^2 + 14s + 7 = (s + 3.80)(s + 2.45)(s + 0.75) \quad (8)$$

with equation (8) means that on inverting the Laplace transform the expressions for u_n contain exponential terms in -3.80τ, -2.45τ, and -0.75τ [equation (9)].

$$u_n = 1/7 + A_n\exp(-0.75\tau) + B_n\exp(-2.45\tau) + C_n\exp(-3.80\tau) \quad (9)$$

Values of the coefficients A_n, B_n, and C_n are given in Table 4 for each shift mechanism. For each site the same three numbers are found in each of the three mechanisms. The last row shows that the boundary condition at $\tau = 0$ is fulfilled for each site. It is also true that summing all u_n, since $\Sigma u_n = 1.00$, then for each row in Table 4, $2X_1 + 2X_2 + 2X_3 + X_7$ where X is A, B, or C must equal zero. This is found to be the case.

TABLE 3

Values of a_n, b_n, and c_n in equations (4)—(7)

	n	1	2	3	7
[1,2]	a	2	1	1	2
	b	7	6	5	8
	c	4	4	3	5
[1,3]	a	1	3	2	2
	b	4	9	6	7
	c	4	4	3	5
[1,5]	a	1	0	0	1
	b	5	1	1	5
	c	4	4	3	5

TABLE 4

Values of A_n, B_n, and C_n for equation (9)

	n	1	2	3	7
[1,2]	A	0.009	−0.003	−0.013	0.014
	B	−0.052	−0.209	0.145	0.232
	C	−0.100	0.069	−0.025	0.111
[1,3]	A	−0.100	0.069	−0.025	0.111
	B	0.009	−0.003	−0.013	0.014
	C	−0.052	−0.209	0.145	0.232
[1,5]	A	−0.052	−0.209	0.145	0.232
	B	−0.100	0.069	−0.025	0.111
	C	0.009	−0.003	−0.013	0.014
$A + B + C + \frac{1}{7}$		0.000	0.000	0.250	0.500

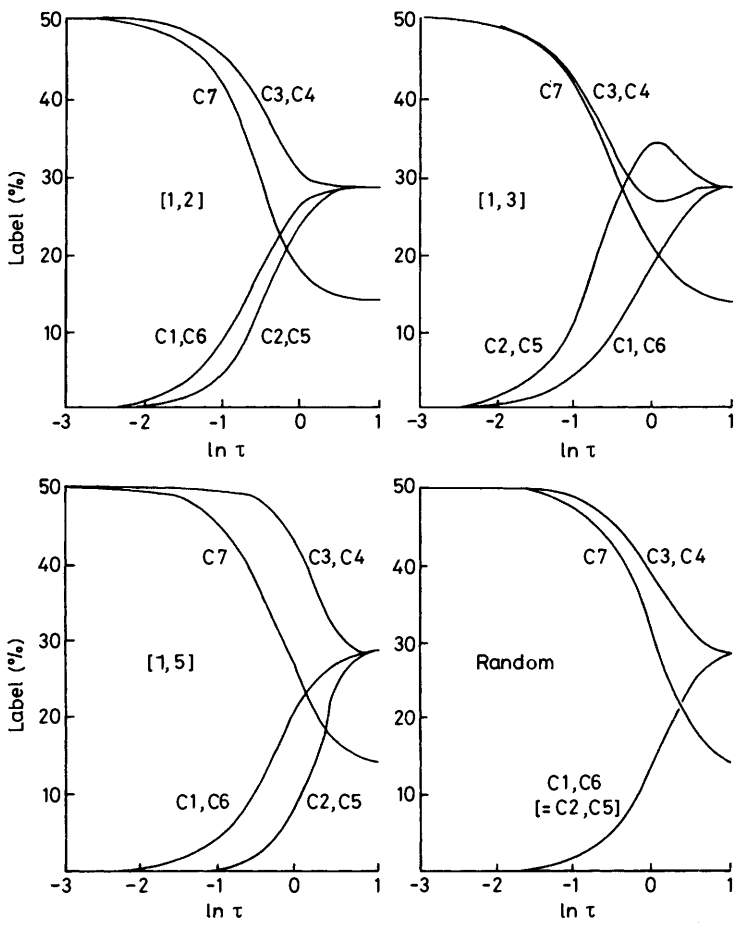


FIGURE 1 The rearrangement of ^{13}C label with time by the four possible mechanisms calculated according to the text

Substitution from Table 4 in equation (9) allows one to calculate u_n as a function of τ to give the results displayed in Figure 1. These are plotted as a function of ln t so that experimental data plotted as a function of ln t may be compared with the theoretical results by simply shifting one graph on top of the other.

For the random mechanism the same approach is used, but the algebra is simpler. We find that equations (10)—(12) hold. Each mechanism gives rise to a very characterestic set of changes in signal intensity (Figure 1). For a [1,2] shift C-7 decays faster than C-3, and C-1 is enriched substantially faster than C-2, the maximum ratio of the latter being *ca.* 2 : 1. Near the reaction half-time (ln$\tau \sim 0$) C-1, -2, and -3 have rather similar intensities. A [1,5] shift mechanism is strikingly different in the first 20—30% of reaction, since almost all the flux is from C-7 to C-1, with little change in the intensity of C-3 and only slight enrichment of C-2. This pattern persists to the half-time of the reaction and when the intensities of C-1 and -7 are equal, C-2 has attained only about half that value and C-3 remains much greater. The [1,3] shift mechanism shows rather interesting behaviour, in that C-3 and -7 decrease at similar rates with selective enrichment of C-2 which steadily increases to a maximum near the half-time to equilibrium. This is because isotopic label is fed to site 2 from two of the initially substituted sites, 4 and 7, in the early stages of reaction by a [1,3] shift mechanism whereas site 1 only receives isotope from site 3. The random mechanism gives a simple steady redistribution, as expected.

$$u_1 = u_2 = \tfrac{1}{7}[1 - \exp(-7\tau)] \quad (10)$$

$$u_3 = u_1 + \tfrac{1}{4}\exp(-7\tau) \quad (11)$$

$$u_7 = u_1 + \tfrac{1}{2}\exp(-7\tau) \quad (12)$$

Mechanisms of Degenerate Rearrangement.—The experimental data given in Table 2 may be conveniently represented in the manner of Figure 2 in which the label distribution at C-1 is plotted against that at C-2. This very clearly shows that rhodium complex (9) rearranges by a random mechanism, and that only a [1,5] shift accurately describes the changes observed in (8). Figure 3 compares all the data for (8) in Table 2 with the calculated lines from theoretical treatment of the [1,5] mechanism.

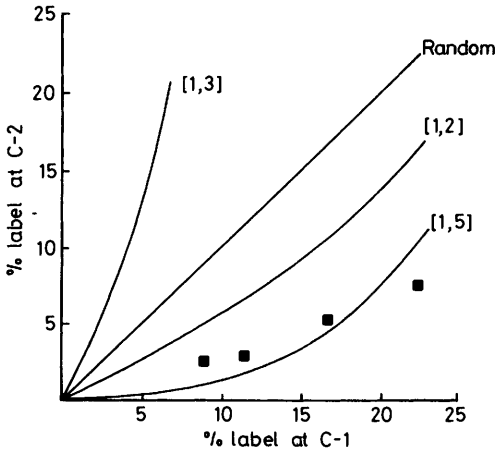


FIGURE 2 Redistribution of ^{13}C label in complex (8) to C-1 and -2 on thermolysis according to the four different shift mechanisms with experimental data included. ■, experimental points

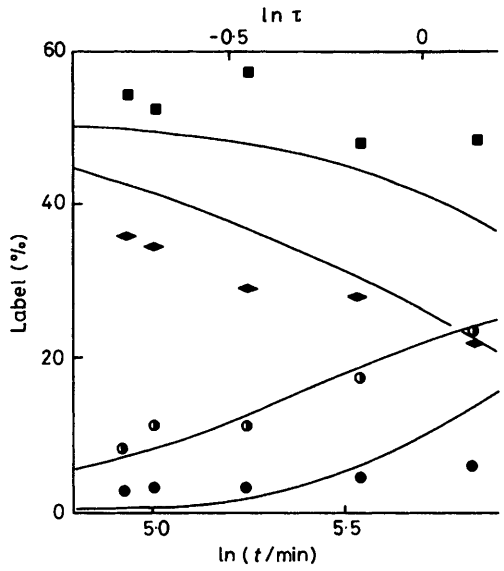
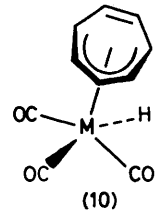


FIGURE 3 Theoretical and experimental evolution of the label distribution in (8) according to the [1,5] shift mechanism. ■, C-3, C-4; ◆, C-7; ◑, C-1, C-6; ●, C-2, C-5

A reasonable fit is found, given the inherent experimental error. This confirms that the time-course of the data for all four positions in Table 2 follows that predicted for the [1,5] shift. From the match between the τ and t scales we find that $k = 5.7 \times 10^{-5}$ s^{-1}.

Sigmatropic shifts in ligated polyenes occur by reversible hydride migration to the metal. To preserve an 18-electron configuration, the intermediate required in rearrangement of (8) is the tricarbonyl hydride (10). A



(10)

rapid fluxional process, for which good analogies exist,[6] would make all carbon atoms of the ring equivalent prior to return of the hydride. Alternatively, a rotation about the ring–metal axis would make it possible for hydride to return with net [1,5] sigmatropic shift. The same result may be brought about by a pseudorotatory motion of the tricarbonyl hydride moiety. Whatever the detailed pathway, it seems that the internal reorganisation leading to rearrangement occurs considerably faster than any fluxional movement of the ring.

In the case of (9) hydride migration is random. Since the starting material is a 16-electron co-ordinatively unsaturated complex, the intermediate may have a η^3-allyl

or η^5-pentadienyl structure with a low energy barrier between the two (Scheme 1). This evidently enables the fluxional process to prevail over hydride return.

We had intended to examine the corresponding labelled cycloheptatriene iron tricarbonyl since consideration of rearrangement pathways involving 18-electron intermediates suggests a possible preference for a [1,3] shift. On learning of Brookhart's unpublished work [15] this was not pursued.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R32 spectrometer and ^{13}C n.m.r. spectra on a Bruker WH 90 machine. All air-sensitive components were handled and stored under dry nitrogen.

^{13}C-Labelled Cycloheptatriene.—[^{13}C]Benzoic acid was prepared from phenylmagnesium bromide and $^{13}CO_2$ according to published procedures,[10] and converted into [1'-^{13}C]-3-hydroxymethylcyclohexa-1,4-diene, b.p. 65 °C at 0.7 mmHg, by successive reduction with sodium in ammonia [16] and ethereal lithium aluminium hydride.

The alcohol (1.17 g, 0.0205 mol) was dissolved in dry pyridine (10 ml) together with freshly recrystallised toluene-*p*-sulphonyl chloride (2.6 g, 0.0135 mol). The flask was set aside at 5 °C for 48 h. After dilution with ether (15 ml) the reaction mixture was washed successively with ice-cold hydrochloric acid (1M, 15 ml), distilled water (5 × 20 ml), and finally with aqueous nickel chloride until no blue colour was apparent in the aqueous washings. The solution was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. [1'-^{13}C]-3-*p*-Tolylsulphonyloxymethylcyclohexa-1,4-diene remained as a yellow oil (3.74 g, 68% from two batches). This was dissolved in glacial acetic acid (60 ml) containing NaH_2PO_4 (4.2 g). The flask was fitted to a small rotary evaporator (Buchi M) arranged to distil out cycloheptatriene as it was formed. The reaction vessel was maintained at an average temperature of 93 °C for 6 h. A pressure of 550 mmHg was maintained which allowed the solution to distil at a rate of *ca.* 1 drop min^{-1}, the distillate being collected in an ice-cooled receiver. Every hour the pressure was briefly reduced to 250 mmHg so that 1 ml of distillate was rapidly collected. On completion of reaction the distillate was neutralised with 6M-KOH and centrifuged. The upper layer was removed, centrifuged again, and transferred to a glass vial which was subsequently sealed. There was thus obtained [3,7-$^{13}C_2$]cyclohepta-1,3,5-triene (0.56 g, 42%). The ^{1}H n.m.r. spectrum showed that 6% of toluene was present, and the ^{13}C n.m.r. spectrum (CD_2Cl_2) confirmed the labelling pattern, δ 131.0 (C-3*), 126.8 (C-2), 121.6 (C-1), and 28.3 (C-7*) p.p.m.

[3,7-$^{13}C_2$]Cycloheptatrienetricarbonylmolybdenum.—Tris-acetonitriletricarbonylmolybdenum [11] [from hexacarbonylmolybdenum (1.0 g) and excess of acetonitrile] was refluxed with [^{13}C]cycloheptatriene (0.24 g) in C_6H_{14} for 3 h in a Schlenk tube under nitrogen. After this time the solution was filtered into a second Schlenk tube, and the volatile portion of the filtrate distilled back into the first vessel *in vacuo*. The reaction mixture was then refluxed for a further 3 h and filtered again into the second Schlenk tube. The solvent was removed *in vacuo* and the residue sublimed at 70 °C and 0.05 mmHg giving *[3,7-$^{13}C_2$]cycloheptatrienetricarbonylmolybdenum* (0.347 g, 49%) as red crystals, δ (C_6D_6) 102.3 (C-2), 97.6 (C-3*), 60.1 (C-1), and 27.4 (C-7*) p.p.m.

[3,7-$^{13}C_2$]Cycloheptatriene-η^4(1—2, 5—6)rhodium(I) Acetylacetonate.—Bis-ethylenerhodium acetylacetonate was prepared by the published procedure.[17] To a sample of the complex (0.281 g, 0.0011 mol) in ether (10 ml) and hexane (10 ml) was added cycloheptatriene (0.11 g, 0.0012 mol, freshly distilled) and the solution stirred at 0 °C for 8 h. The mixture was filtered three times under nitrogen to remove all traces of suspended solid, and solvent was then removed *in vacuo*. The residue was dissolved in petroleum (10 ml; b.p. 30—40 °C) and filtered twice under nitrogen. The product was recrystallised at −45 °C to give *[3,7-$^{13}C_2$]-cycloheptatriene-η^4(1—2, 5—6)rhodium(I) acetylacetonate* (0.230 g, 72%), δ (C_6D_6) 138.1 (C-3*), 75.6 (C-2, J_{CRh} 14 Hz), 50.2 (C-1, J_{CRh} 9 Hz), and 29.9 (C-7*) p.p.m.

Thermolysis Experiments.—In the case of cycloheptatrienetricarbonylmolybdenum, samples of complex (0.09 g) were dissolved in [$^2H_6$]benzene (1 ml) and transferred under nitrogen to $NaHCO_3$-washed Pyrex tubes which were sealed prior to thermolysis at 95—100 °C. The solution was in each case filtered into a 10 mm n.m.r. tube and a small quantity of [$^2H_6$]benzene added prior to accumulation of spectra. The ^{13}C content of each sample was analysed by plotting the spectrum on a sweep width of 5 Hz cm^{-1} and analysing by triangulation. Simulation with a Dupont curve analyser gave essentially similar results.

Samples of cycloheptatrienerhodium(I) acetylacetonate were thermolysed directly in 10 mm n.m.r. tubes prepared by $NaHCO_3$ washing.

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