Homogeneous Catalysis of Olefin Isomerisation. Part IV.[1] The Isomerisation of Pent-1-ene catalysed by Solutions of $IrH(CO)(PPh_3)_3$, $IrHCl_2(PEt_2Ph)_3$, $IrCl(CO)(PPh_3)_2$, $IrCl(O_2)(CO)(PPh_3)_2$, and of $PtH(SnCl_3)(PPh_3)_2$

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The isomerisation of pent-1-ene to pent-2-ene at 80 °C is catalysed by solutions of (i) $IrH(CO)(PPh_3)_3$, (ii) $IrHCl_2(PEt_2Ph)_3$, (iii) $IrCl(CO)(PPh_3)_2$ or $IrCl(O_2)(CO)(PPh_3)_2$ each in the presence of an oxygen source, and (iv) $PtH(SnCl_3)(PPh_3)_2$ in benzene. Systems (i), (ii), and (iv) catalyse the preferential formation of *cis*-pent-2-ene (initial *cis*:*trans* ratios typically 2·0 to 3·5) whereas (iii) provides preferential formation of *trans*-pent-2-ene (initial *cis*:*trans* ratio *ca.* 0·6).

The isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by (i), (iii), and (iv) is reported. Intermolecular hydrogen transfer typical of isomerisation *via* the formation of pentyl complexes was observed in each case. Stepwise movement of the double bond occurred in systems (i) and (iii), whereas multiple movement was observed in (iv). The relative probabilities of the three elementary reactions (*viz*: formation of pent-1-yl complex, formation of a pent-2-yl complex, and isomerisation) are calculated for each system.

Gross variations of the *cis*:*trans* ratio are interpreted in terms of the presence or absence of steric interaction between bulky ligands and the pent-2-yl group.

ISOMERISATION of pent-1-ene to pent-2-ene catalysed by complexes of nickel,[1] osmium,[1] and ruthenium,[2] has been described earlier. The intermediates in these reactions were alkylmetal complexes. Preferential formation of *cis*-pent-2-ene occurred, and deuterium-labelled pent-1-ene was used to demonstrate that only a single movement of the double bond took place during one period of co-ordination of the C_5-entity to the catalytically active complex. Steric hindrance by bulky ligands to rotation of the secondary pentyl group about the carbon–metal bond limited the isomerisation rate.

TABLE 1

Isomerisation of pentene catalysed by complexes of iridium and of platinum

[Pentene] = 1·0M. Temperature, 80 °C. Solvent, benzene

Complex	Complex concentration/ mM	Oxygen source	Reactant	Initial rate of reaction/ 10^{-4} mol l^{-1} min^{-1}	$\frac{[cis\text{-Pent-2-ene}]}{[trans\text{-Pent-2-ene}]}$ [a]
$IrH(CO)(PPh_3)_3$	1·01	None	Pent-1-ene	4·2	2·0
$IrH(CO)(PPh_3)_3$	2·02	None	Pent-1-ene	5·0	2·0
$IrH(CO)(PPh_3)_3$	2·02	None	*cis*-Pent-2-ene	0·9	
$IrHCl_2(PEt_2Ph)_3$	1·84	None	Pent-1-ene	38	3·5
$IrCl(CO)(PPh_3)_2$	4·90	$O_2(g)$ [b]	Pent-1-ene	15·0	0·61
$IrCl(O_2)(CO)(PPh_3)_2$	4·80	$O_2(g)$ [b]	Pent-1-ene	20·0	0·63
$IrCl(O_2)(CO)(PPh_3)_2$	1·76	$O_2(g)$ [b]	Pent-1-ene	12·5	0·60
$IrCl(CO)(PPh_3)_2$	1·60	$t\text{-}C_4H_9O_2H$ [c]	Pent-1-ene	14·0	0·62
$IrCl(O_2)(CO)(PPh_3)_2$	4·80	$O_2(g)$ [b]	*cis*-Pent-2-ene	10·6	
$PtH(SnCl_3)(PPh_3)_2$	1·04	None	Pent-1-ene	3·7	3·0

[a] Initial value. [b] Oxygen pressure *ca.* 1 atmosphere. [c] [$t\text{-}C_4H_9O_2H$] = 30 mM.

Investigations reported here have revealed (i) two further reactions which behave similarly to those catalysed by nickel and osmium complexes,[1] (ii) an example of isomerisation with multiple movement of the double bond, and (iii) a reaction giving preferential formation of pent-2-ene in the *trans*-configuration.

EXPERIMENTAL

$IrH(CO)(PPh_3)_3$,[3] $IrHCl_2(PEt_2Ph)_3$,[4] $IrCl(CO)(PPh_3)_2$,[5] $IrCl(O_2)(CO)(PPh_3)_2$,[6] and $PtH(SnCl_3)(PPh_3)_2$ [7] were prepared as described in the literature.

Isomerisation at 80 °C and analyses were carried out as described earlier [1,2] except that, when required, about one atmosphere pressure of oxygen was admitted to the reaction vessel after the addition of all other components.

RESULTS

$IrH(CO)(PPh_3)_3$ in benzene isomerised pent-1-ene slowly at 80 °C to give pent-2-ene having an initial *cis* : *trans* ratio of 2·0 [Figure (a)]. Geometrical isomerisation of the product was very slow; thermodynamic equilibrium proportions of the pentenes were not obtained after 130 h. However, when *cis*-pent-2-ene was used as reactant, the initial rate of its removal was about one fifth of that recorded for pent-1-ene (Table 1). Thus, during pent-1-ene isomerisation, the reactant severely inhibited geometrical isomerisation of pent-2-ene. The rate of pent-1-ene isomerisation did not increase in proportion to the nominal concentration of this complex (Table 1).

Solutions in benzene of $IrHCl_2(PEt_2Ph)_3$ of configuration (A) exhibited greater catalytic activity than those of the five-co-ordinate iridium carbonyl hydride described above [Figure (b) and Table 1]. The complex underwent re-

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[1] Part III, D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1928.

[2] Part II, D. F. Ewing, B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1287.

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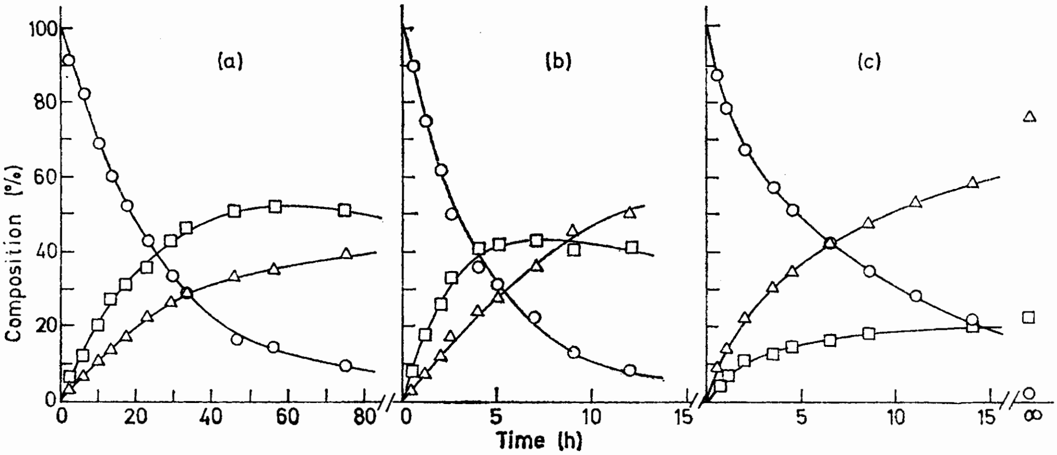
[4] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.

[5] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.

[6] L. Vaska, *Science*, 1963, **140**, 809.

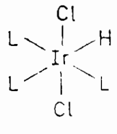
[7] J. C. Bailar, jun., and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.

arrangement in solution and a white solid was precipitated which was identified as (B) from its i.r. spectrum.[4] If precipitation occurred the isomerisation rate was reduced. Figure (b) describes the course of the isomerisation; the *cis* : *trans* ratio was 3·6 initially, and geometrical isomerisation of the product was fairly rapid.

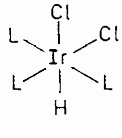


Pent-1-ene isomerisation at 80 °C. Variation of pentene composition with time. Catalyst solutions: (a) $IrH(CO)(PPh_3)_3$, 2·02 mM in benzene; (b) $IrHCl_2(PEt_2Ph)_3$, 1·80 mM in benzene; (c) $IrCl(O_2)(CO)(PPh_3)_2$, 3·01 mM in benzene in the presence of one atmosphere of oxygen. [Pentene] = 1·0M. ○ = Pent-1-ene; □ = *cis*-pent-2-ene; △ = *trans*-pent-2-ene

$IrCl(CO)(PPh_3)_2$ in benzene isomerised pent-1-ene at 80 °C when gaseous oxygen or t-butyl hydroperoxide was present [Figure (c), Table 1]. In this reaction, *trans*-pent-2-ene was preferentially formed; the *cis* : *trans* ratio was 0·6 initially and this value fell steadily as reaction progressed. Similar catalysis was observed when the oxygen adduct $IrCl(O_2)(CO)(PPh_3)_2$ was dissolved in benzene; the activity of this solution was also increased by the addition of oxygen gas to the reaction vessel. The isomerisation rate did not increase in proportion to the nominal concentration of the oxygen complex (Table 1). Reactions in the presence of oxygen gas were not affected by the addition of radical inhibitors such as *o*-methoxyphenol (19 mM) or hydroquinone (57 mM). The rate of isomerisation in the presence of 30 mM t-butyl hydroperoxide was similar to that observed in reactions in the presence of about one atmosphere of gaseous oxygen (Table 1). When triphenylphosphine (1·6 mM) was added to a solution of pent-1-ene containing $IrCl(CO)(PPh_3)_2$ (1·6 mM) and t-butyl hydroperoxide (30 mM) no isomerisation of pentene occurred at 80 °C. *cis*-Pent-2-ene isomerisation was catalysed by solutions of the oxygen adduct at about half the rate of pent-1-ene isomerisation (Table 1).



(A)



(B)

(L = PEt_2Ph)

$PtH(SnCl_3)(PPh_3)_2$ in benzene (1·0 mM) or in benzene–propanol (3 : 2) mixtures catalysed pent-1-ene isomerisation slowly at 80 °C. The initial rate of pent-1-ene removal was increased by the admission of gaseous hydrogen to the reaction vessel, or by the addition of stannous chloride but was diminished by the addition of propanol. The initial *cis* : *trans* ratio in the product was about 3·0, and geometric isomerisation of the products was slow.

Isomerisation of deuterium-labelled pentene was investigated in order to obtain detailed information about the mechanism of double bond movement, and in particular to determine whether the reactions described in Figures (a) (preferential formation of *cis*-olefin) and (c) (preferential formation of *trans*-olefin) occurred by similar or by different mechanisms. Accordingly, [1,2-$^2H_2$]pent-1-ene isomerisation catalysed by solutions of $IrH(CO)(PPh_3)_3$ [reaction (A)], $IrCl(CO)(PPh_3)_2$ under oxygen [reaction (B)], and of $PtH(SnCl_3)(PPh_3)_2$ [reaction (C)], is described in detail in Table 2. Redistribution of deuterium in the reactant occurred, being most extensive for reaction (B). Intermolecular hydrogen transfer occurred in each case, with the result that the deuterium number of the pent-1-ene fell as each reaction progressed, and the pent-2-ene isomers each contained more deuterium than the original reactant. The loss of deuterium from pent-1-ene occurred at C-2, and isomerisation was accompanied by an accumulation of deuterium at C-1 in the pent-2-ene. Pent-2-ene formed in the iridium-catalysed reactions contained little or no deuterium at C-3, C-4, or C-5 (the absence of deuterium at C-3 was inferred from the ^1H n.m.r. splitting pattern for hydrogen located at C-4 [1]). In contrast, deuterium was present at every carbon atom of pent-2-ene formed in the platinum-catalysed reaction. No deuterium was incorporated into the triphenylphosphine ligands during isomerisation in any of these systems.

A brown solid was obtained after removal of solvent and olefin by vacuum distillation from the brown oxygen-saturated reaction mixtures that had originally contained $IrCl(CO)(PPh_3)_2$. The i.r. spectrum of this residue was similar to that of the dark green solid obtained by reacting $IrCl(CO)(PPh_3)_2$ with excess of t-butyl hydroperoxide in benzene at 25 °C. Each spectrum contained (i) an absorption at 2040 cm^{-1} attributable to a carbonyl group, indicating the presence of an iridium(III) complex,[8] and (ii) absorptions at 1120 and 1190 cm^{-1} due to triphenylphosphine oxide.[9] There was no evidence from these spectra for the

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[8] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[9] J. C. Sheldon and S. Y. Tyree, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 2117.

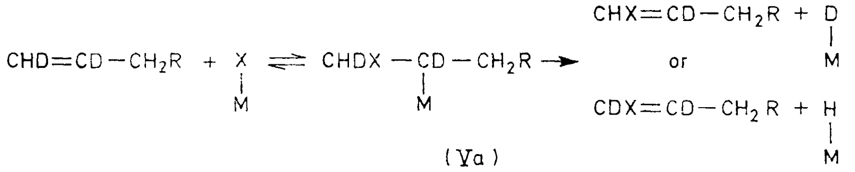
TABLE 2

Distribution and location of deuterium in pentene during isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by solutions in benzene of $IrH(CO)(PPh_3)_3$ [reaction (A)], of $IrCl(CO)(PPh_3)_2$ [reaction (B)], and of $PtH(SnCl_3)(PPh_3)_2$ [reaction (C)]

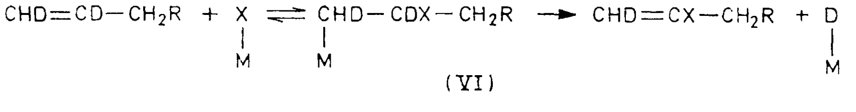
[Pent-1-ene] = 1·0M initially. [Complex] = 2·02 mM (A), 2·94 mM (B), or 1·70 mM (C). Temperature, 80 °C. Volume of solution = 11 ml. Oxygen pressure = 1 atmosphere (B) or zero (A,C)

Reaction	Olefin	Extent of isomerisation (%)	Deuterium distribution (%) C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$	$C_5H_5D_5$ [a]	D.N.[b]	Mean deuterium number at each carbon atom [c] C-1	C-2	C-3	C-4	C-5
	Pent-1-ene	0	0·4	2·6	96·8	0·2	0·0	0·0	1·97	0·97	1·00	0·00	0·00	0·00
(A)	Pent-1-ene	12	0·2	13·0	83·1	3·6	0·1	0·0	1·90	1·07	0·85	0·00	0·00	0·00
		d	*0·4*	*11·8*	*84·2*	*3·6*	*0·0*	*0·0*	*1·91*	*0·97*	*0·94*	*0·00*	*0·00*	*0·00*
		51	1·7	34·4	56·2	7·3	0·4	0·0	1·70	0·96	0·68	0·00	0·00	0·06
		d	*7·1*	*34·7*	*48·3*	*9·9*	*0·0*	*0·0*	*1·61*	*0·91*	*0·70*	*0·00*	*0·00*	*0·00*
	cis-Pent-2-ene	12	0·0	6·3	54·9	37·4	1·4	0·0	2·34	1·26	1·04	0	0·04	0·00
		d	*0·5*	*3·9*	*51·4*	*43·2*	*1·0*	*0·0*	*2·40*	*1·43*	*0·97*	*0·00*	*0·00*	*0·00*
		51	0·3	11·6	47·1	38·2	2·8	0·0	2·32	1·50	0·78	0	0·00	0·04
		d	*2·1*	*15·3*	*47·1*	*32·2*	*3·3*	*0·0*	*2·19*	*1·37*	*0·82*	*0·00*	*0·00*	*0·00*
	trans-Pent-2-ene	51	0·2	11·7	47·2	38·5	3·1	0·0	2·32					
(B)	Pent-1-ene	12	2·3	22·3	59·0	16·2	0·2	0·0	1·90	1·11	0·72	0·02	0·00	0·05
		e	*2·2*	*23·4*	*58·7*	*16·7*	*0·0*	*0·0*	*1·90*	*1·02*	*0·88*	*0·00*	*0·00*	*0·00*
		36	6·4	30·8	44·4	18·0	0·4	0·0	1·75	1·11	0·57	0·04	0·04	0·00
		e	*9·1*	*33·2*	*41·2*	*16·5*	*0·0*	*0·0*	*1·65*	*1·02*	*0·63*	*0·00*	*0·00*	*0·00*
	cis-Pent-2-ene	36	2·3	14·9	37·8	33·0	12·0	0·0	2·38					
	trans-Pent-2-ene	36	2·1	14·2	37·8	34·8	11·1	0·0	2·39	1·43	0·83	0	0·07	0·06
		e	*3·0*	*16·7*	*37·2*	*33·3*	*9·8*	*0·0*	*2·30*	*1·56*	*0·74*	*0·00*	*0·00*	*0·00*
(C)	Pent-1-ene	18	0·4	21·7	72·3	5·4	0·2	0·0	1·83	1·05	0·66	0·08	0·02	0·02
		f	*0·8*	*17·8*	*77·2*	*4·2*	*0·0*	*0·0*	*1·85*					
		56	3·6	41·2	46·4	8·3	0·5	0·0	1·61	1·02	0·57	0·00	0·00	0·02
		f	8·5	43·8	41·0	6·7	0·0	0·0	1·46					
	cis-Pent-2-ene	18	0·0	5·2	37·1	55·5	2·1	0·1	2·55	1·35	0·83		0·19	0·18
		f	*0·1*	*4·3*	*39·1*	*55·0*	*1·5*	*0·0*	*2·54*					
		56	0·6	14·7	42·6	38·9	3·1	0·1	2·30	1·40	0·74		0·02	0·14
		f	*2·1*	*19·0*	*44·4*	*31·5*	*3·0*	*0·0*	*2·43*					
	trans-Pent-2-ene	18	0·0	5·8	36·4	54·4	3·3	0·1	2·56	1·22	0·88		0·19	0·27
		56	0·4	13·9	41·6	39·0	4·9	0·2	2·35	1·27	0·63		0·16	0·29

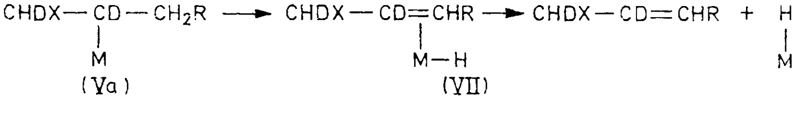
[a] More highly deuteriated pentenes not observed. [b] D.N. = deuterium number of the pentene sample. [c] Values uncertain to ±0·05. [d] Calculated distributions using $p = 0·25$; $s = 0·70$; $i = 0·05$ [e] Calculated distributions using $p = 0·35$; $s = 0·45$; $i = 0·20$. [f] Calculated distributions using $p = 0·68$; $s = 0·18$; $i' = 0·14$.



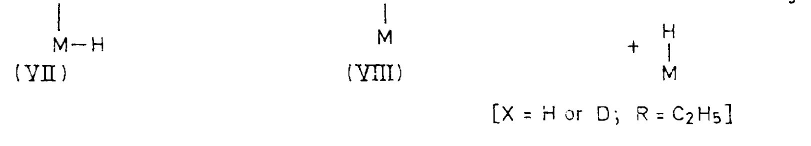
$$\mathrm{CHD{=}CD{-}CH_2R} + \underset{\mathrm{M}}{\mathrm{X}} \rightleftharpoons \underset{(\mathrm{Va})}{\mathrm{CHDX{-}}\underset{\mathrm{M}}{\mathrm{CD}}\mathrm{{-}CH_2R}} \longrightarrow \begin{array}{c} \mathrm{CHX{=}CD{-}CH_2R} + \underset{\mathrm{M}}{\mathrm{D}} \\ \text{or} \\ \mathrm{CDX{=}CD{-}CH_2R} + \underset{\mathrm{M}}{\mathrm{H}} \end{array} \qquad (3)$$



$$\mathrm{CHD{=}CD{-}CH_2R} + \underset{\mathrm{M}}{\mathrm{X}} \rightleftharpoons \underset{(\mathrm{VI})}{\underset{\mathrm{M}}{\mathrm{CHD}}\mathrm{{-}CDX{-}CH_2R}} \longrightarrow \mathrm{CHD{=}CX{-}CH_2R} + \underset{\mathrm{M}}{\mathrm{D}} \qquad (4)$$



$$\underset{(\mathrm{Va})}{\mathrm{CHDX{-}}\underset{\mathrm{M}}{\mathrm{CD}}\mathrm{{-}CH_2R}} \longrightarrow \underset{(\mathrm{VII})}{\mathrm{CHDX{-}}\underset{\mathrm{M{-}H}}{\mathrm{CD}}\mathrm{{=}CHR}} \longrightarrow \mathrm{CHDX{-}CD{=}CHR} + \underset{\mathrm{M}}{\mathrm{H}} \qquad (5)$$



$$\underset{(\mathrm{VII})}{\mathrm{CHDX{-}}\underset{\mathrm{M{-}H}}{\mathrm{CD}}\mathrm{{=}CHR}} \rightleftharpoons \underset{(\mathrm{VIII})}{\mathrm{CHDX{-}CHD{-}}\underset{\mathrm{M}}{\mathrm{CHR}}} \longrightarrow \mathrm{CHDX{-}CHD{-}CH{=}CH{-}CH_3} + \underset{\mathrm{M}}{\mathrm{H}} \qquad (8)$$

[X = H or D; R = C_2H_5]

presence of hydrido-complexes or of complexes containing co-ordinated molecular oxygen. The dark green solid gave a brown solution when dissolved in benzene at 80 °C.

DISCUSSION

Reactions Catalysed by Iridium Complexes.—The behaviour of solutions of IrH(CO)(PPh$_3$)$_3$ and of IrHCl$_2$(PEt$_2$Ph)$_3$ as catalysts for pent-1-ene isomerisation is, in general, similar to that of solutions of the rhodium analogues,[10] except that the iridium catalysts exhibit lower activity per mole of complex dissolved. This lower activity may be due to stronger bonding of phosphine ligands to iridium, by comparison to rhodium, thereby leading to the establishment of a lower concentration of catalytically active complex by dissociation of the original compound. Alternatively, the lower activity may be a reflection of the greater stability of hydrido- or alkyl-complexes of iridium compared with rhodium. When the concentration of IrH(CO)(PPh$_3$)$_3$ was doubled (Table 1) there was only a small increase in rate, which is consistent with the formation of catalytically active complexes by ligand dissociation.

Table 2 shows that isomerisation was accompanied by intermolecular transfer of hydrogen and of deuterium, and that deuterium transfer from C-2 to C-1 occurred. No appreciable transfer of deuterium to C-3, C-4, or C-5 in pent-1-ene or in pent-2-ene took place during the initial stages of reaction. Thus, only a single movement of the double bond occurred during one period of co-ordination of the C$_5$-entity to the catalytically active complex. The same deuterium movements were reported for isomerisation catalysed by a nickel complex and by an osmium complex [1] for which equations (3)—(5) of the following mechanism were proposed (numbering of equations and intermediates follows ref. 1). Displacement of pent-2-ene from (VII) [equation (5)] must be rapid, otherwise the process shown in equation (8), involving the formation of a pent-3-yl complex, would occur and would result in the appearance of deuterium in the ethyl group of pent-2-ene.

It was shown earlier [1] that the location and distribution of deuterium in the pentenes can be calculated provided that the hydrocarbon entity undergoes only one conversion of the type pentene ⟶ pentyl ⟶ pentene before being displaced from the catalytically active centre. The parameter p defines the probability that pent-1-ene will undergo exchange at C-2 by equation (4); s defines the probability that pent-1-ene will undergo exchange at C-1 by equation (3); and i defines the probability that isomerisation will occur by equation (5). Table 2 shows calculated distributions and locations for deuterium which are in acceptable agreement with the observed values. [Strictly, calculations cannot be made for reaction (C) since the multiple movement of the double bond transgresses the basic assumption of the calculation. However, provided the intermediates in equation (8) do not exchange hydrogen or deuterium with the system, the procedure continues to provide the distribution (but not now the location) of deuterium in the pent-2-ene. Where this additional assumption is made, the isomerisation parameter is denoted by i'.] Values of p, s, and i obtained for isomerisation catalysed by the solution of IrH(CO)(PPh$_3$)$_3$ are closely similar to those reported [1] for isomerisation catalysed by benzene solutions of OsHCl(CO)(PPh$_3$)$_3$, *viz* :

	p	s	i
Ir catalyst	0·25	0·70	0·05
Os catalyst	0·20	0·76	0·04

Thus it is likely that these compounds are converted by reaction with the solvent to structurally similar catalytic species.

Benzene solutions of IrCl(CO)(PPh$_3$)$_2$ became catalytically active only in the presence of an oxygen source. The isomerisation rate and the *cis* : *trans* ratio in the product were similar irrespective of whether the oxygen source was O$_2$ or t-butyl hydroperoxide. The movement of deuterium, using this activated complex as catalyst [reaction (B) of Table 2], was basically similar to that observed with the iridium carbonyl hydride complex just discussed [reaction (A)], and can be accounted for only in terms of a mechanism involving pentyl intermediates. Thus it is concluded that the catalytically active complexes were hydrido-complexes which were stable in the presence of the oxygen sources. Calculations (Table 2) show that equations (3)—(5) describe the mechanism acceptably when $p = 0{\cdot}35$, $s = 0{\cdot}45$, and $i = 0{\cdot}20$. The mechanism of formation of the proposed catalytically active hydrido-complexes from IrCl(CO)(PPh$_3$)$_2$ is not clear. However IrHCl$_2$(PEt$_3$)$_3$ is formed from IrCl$_3$(PEt$_3$)$_3$ when the latter reacts with olefin provided an oxygen source (in this case olefin hydroperoxide) is available.[11] Further studies of such processes are required.

It was hoped that the brown solid extracted from reaction (B) would provide information concerning the nature of the catalytically active complex. The material isolated appeared to be a carbonyl complex of Ir^{III} containing one or more triphenylphosphine oxide ligands. Absorptions due to hydride ligands were not detected from which we conclude that, if the catalyst survived the vacuum distillation, it constituted only a very small proportion of the isolated material. The formation of complexes having triphenylphosphine oxide ligands is not unexpected, since solutions of IrCl(CO)(PPh$_3$)$_2$ are known to catalyse the oxidation of triphenylphosphine.[6,12]

The cis : trans *Ratio in the Product.*—Earlier,[1] and in Tables 1 and 2, it is shown that preferential formation of the *cis*-isomer is associated with a situation in which $s \gg i$. The unusual preferential formation of the *trans*-isomer [reaction (B), Table 2] is accompanied by s and i being of comparable magnitude. The condition $s \gg i$ has been interpreted to mean that rotation about the

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[10] C. J. Anspack, Ph.D. Thesis, University of Hull, 1971.

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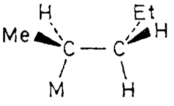
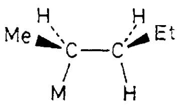
carbon–metal bond in the pent-2-yl complex (Va) is severely restricted,[1] *i.e.* exchange of hydrogen for deuterium at C-1 (which does not require rotation about the carbon–metal bond) proceeds more rapidly than hydrogen atom abstraction from C-3 (which does require such a rotation). Thus we infer that the experimental conditions achieved in reaction (B) were such that the restriction to rotation about the carbon–metal bond in (Va) was much reduced by comparison with that achieved in reaction (A).

We propose the following hypothesis to explain the observed *cis* : *trans* ratio of products obtained in this, and other, homogeneously catalysed isomerisations. Consider the secondary pentyl complex (Va), which we write as $ML_5(C_5H_{11})$, and similar alkyl complexes. There are two sources of steric interactions that play a part in determining whether the *cis*- or the *trans*-form of the internal olefin is formed. First, there are the atomic interactions within the $C_5H_{11}M$ group. These, of course, are always present and will be minimised when the $C_5H_{11}M$ group, immediately before conversion to olefin and metal hydride, has the eclipsed conformation (**A**). This leads, by transfer of the eclipsed hydrogen onto the metal, to *trans*-pent-2-ene. The alternative eclipsed conformation, (**B**), gives *cis*-pent-2-ene. Secondly, there may be atomic interactions between the C_5H_{11} group and the other ligands, L. When these ligands, L, are bulky (*e.g.* PPh_3 molecules) they extend well beyond the metal and the attached alkyl group, and the freedom of the alkyl group is seriously restricted. It is suggested that, in these circumstances, the steric interactions between some ligands L and the pentyl group dominate over those within the pentyl group, the preferred conformation immediately before olefin formation is then that shown in (**B**), and hence *cis*-pent-2-ene is formed. In (**B**) the ethyl group of the pent-2-yl ligand has moved away from the ligands L to give a more compact conformation where it is shielded from these ligands by the methyl group.



(**A**)



(**B**)

Hence we have a consistent interpretation of the *cis* : *trans* ratio in the pent-2-ene. When the catalyst is a triphenylphosphine complex [reaction (A)] the bulky triphenylphosphine ligands interact strongly with the pentyl group, restricting its rotation so that $s \gg i$, and causing it to adopt the compact conformation (**B**) thus providing preferential formation of *cis*-pent-2-ene. However, when the catalyst has triphenylphosphine oxide ligands [as may be the case in reaction (B)] interpolation of oxygen between iridium and phosphorus reduces the steric interaction between the PPh_3 groups and the C_5H_{11} ligand sufficiently to allow rotation about the carbon–metal bond ($s \sim i$) and the adoption by the pentyl ligand of all possible conformations, thus leading to preferential formation of conformation (**A**) and hence of *trans*-pent-2-ene.

This hypothesis that the extent of congestion at the catalytically active site influences the stereospecificity of the reaction is examined further in the following paper.

Reaction Catalysed by the Platinum Complex.—The movements of deuterium during isomerisation, *i.e.* intermolecular hydrogen transfer and deuterium migration from C-2 to C-1, demonstrate that isomerisation proceeded *via* the formation of pentyl complexes. Deuterium redistribution in pent-1-ene occurred in a manner consistent with equations (3) and (4) and the primary act of isomerisation by equation (5). The preferential formation of *cis*-pent-2-ene is in accordance with expectation, based on the previous section, since it is likely that the catalytically active complex contained triphenylphosphine ligands. The presence of deuterium in the ethyl group of initially formed pent-2-ene indicates that multiple movement of the double bond occurred during a single period of co-ordination of the C_5-entity to the catalytically active complex [equations (5) and (8)]. Such multiple movement has not been observed before in olefin isomerisation catalysed by complexes of the noble Group VIII metals; its observation in this case may be related to the well known stability of olefin complexes of platinum.

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