Homogeneous Catalysis of Olefin Isomerisation. Part V.[1] Pent-1-ene Isomerisation catalysed by Solutions of $RuHCl(PPh_3)_3$ and of $RuHCl(CO)(PPh_3)_3$; Variation of the Isomeric Composition of Pent-2-ene and its Attribution to Steric Factors

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Isomerisation of pent-1-ene to pent-2-ene in the range 35 to 80 °C is catalysed by solutions of $RuHCl(PPh_3)_3$ and of $RuHCl(CO)(PPh_3)_3$ in benzene. Preferential formation of *cis*-olefin occurs at higher catalyst concentrations, but a change to preferential *trans*-olefin formation is observed as catalyst concentration is reduced. This change in selectivity, which is not accompanied by a change in mechanism, is attributed to a progressive decongestion of the catalytic site brought about by a gradual increase in the degree of dissociation of the catalyst by loss of triphenylphosphine ligands.

ISOMERISATION of suitable alk-1-enes provides alk-2-ene in *cis* and *trans* forms. The *cis* : *trans* ratio in the product is an important feature of the reaction and it may vary widely, for reasons that have not been well understood. For catalysis by Group VIII metal complexes in solution, the following three generalisations can be made. First, provided isomerisation proceeds *via* the formation of alkyl complexes, and provided the metal complex contains phosphine ligands, preferential formation of *cis*-olefin occurs almost without exception, *e.g.* initial values of the *cis* : *trans* ratio (usually using benzene as solvent) were: acidified $Ni[P(OEt)_3]_4$, 2·3;[2,3] $RuHCl(PPh_3)_3$, 1·6;[4] $RhH(CO)(PPh_3)_3$, 1·5—3·0;[5,6] acidified $[RhCl_2(C_2H_4)_2]_2$, 1·7;[7] $OsHCl(CO)(PPh_3)_3$, 6·0;[2] $IrH(CO)(PPh_3)_3$, 2·0;[1] $IrHCl_2(PEt_2Ph)_3$, 3·5;[1] $PtH(SnCl_3)(PPh_3)_2$, 3·0.[1] Secondly, *trans*-olefin may be the preferred product if the complex does not contain bulky phosphine groups [*e.g.* *cis* : *trans* ratios in the range 0·3 to 0·4 have been observed[8] in catalysis by solutions containing chloroplatinic acid in the presence of stannous chloride and hydrogen, and by solutions of $FeH(CO)_4^-$]. Thirdly, isomerisation *via* the formation of π-allylic intermediates appears to give preferential formation of *trans*-olefin [*e.g.* $Fe_3(CO)_{12}$, 0·35[9]].

The preferential formation of *either* isomer using complexes of iridium was reported in the preceding paper.[1] Preferential *cis*-olefin formation occurred when interactions of the bulky phosphine ligands with the hydrocarbon ligand were important, that is, when the site of catalytic activity was highly congested. (Congestion was detected in terms of restriction to rotation about the carbon–metal bond in the alkyl complex.) Preferential *trans*-olefin formation was associated with a lower extent of congestion, possibly achieved by the conversion of phosphine ligands to phosphine oxide ligands.

Changes in the isomeric composition of the product should accompany other processes that relieve congestion at the catalytically active site. We considered that congestion might be relieved by increasing the extent of dissociation of a complex in solution, this being achieved by decreasing the catalyst concentration. A necessary feature is that at least two species formed by solvolysis of the original complex should be catalytically active for olefin isomerisation. Accordingly, we have examined pent-1-ene isomerisation catalysed by benzene solutions of $RuHCl(PPh_3)_3$ and of $RuHCl(CO)(PPh_3)_3$, and have determined the dependence of the *cis* : *trans* ratio in the product upon the nominal concentration of each complex. Ruthenium systems were chosen because $RuHCl(PPh_3)_3$ undergoes substantial dissociation in benzene.[4]

EXPERIMENTAL

$RuHCl(PPh_3)_3$[10] and $RuHCl(CO)(PPh_3)_3$[11] were prepared by methods described in the literature. Reactions and analyses were carried out exactly as described previously.[1,2,4]

RESULTS AND DISCUSSION

Initial rates of reaction and product compositions for pent-1-ene isomerisation catalysed by benzene solutions of $RuHCl(PPh_3)_3$ and of $RuHCl(CO)(PPh_3)_3$ are shown in Table 1. The first two entries record reasonable agreement between present and previous work.[4] Solutions of $RuHCl(CO)(PPh_3)_3$ exhibited a higher activity per mole of complex dissolved than those of $RuHCl(PPh_3)_3$. The solutions were extremely sensitive to the presence of oxygen, and hence the dependence of rate upon complex concentration is not discussed in detail. In each system, the variation of complex concentration at 80 °C caused a change from preferential *cis*-olefin formation at the higher concentrations to preferential *trans*-olefin formation at the lower.

It was necessary to establish whether these changes of product composition had been accompanied by a

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basic change in reaction mechanism from an addition–abstraction process involving alkyl intermediates (which commonly gives preferential *cis*-olefin formation) to an abstraction–addition process involving π-allylic intermediates (which commonly gives preferential *trans*-olefin formation, see above). Accordingly, the isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by solutions of $RuHCl(CO)(PPh_3)_3$ was examined (see Table 2). [The movements of deuterium during the isomerisation of this olefin catalysed by solutions of $RuHCl(PPh_3)_3$ have been reported in Part II;[4] the complexities were such that further examination in the present context was not undertaken.]

TABLE 1

Pent-1-ene isomerisation: variation of rate of product composition upon complex concentration

Solvent = benzene. [Pentene] = 1·0M. Volume of solution = 11 ml

Complex	Complex concentration/ µM	Temp./ °C	Initial rate of reaction/ mmol l^{-1} min^{-1}	Initial product composition (%) *cis*-Pent-2-ene	Initial product composition (%) *trans*-Pent-2-ene	[*cis*]/[*trans*]
$RuHCl(PPh_3)_3$	1700 [a]	50	16·4	58	42	1·40
	400	50	3·4	52	49	1·06
	1200	80	90	57	43	1·34
	480	80	60	55	45	1·25
	200	80	16·6	49	51	0·96
	140	80	10·5	42	58	0·72
	100	80	10·5	41	59	0·70
	65	80	5·6	36	64	0·57
	40	80	1·7	23	77	0·30
$RuHCl(CO)(PPh_3)_3$	1060	35	38	71	29	2·5
	97	80	130	63	37	1·7
	48	80	30	57	43	1·3
	31	80	64	29	71	0·4
	19	80	6·0	45	55	0·8
	10	80	0·8	9	91	0·1

[a] Previous work (ref. 4).

TABLE 2

Distribution and location of deuterium in pentene during isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by solutions of $RuHCl(CO)(PPh_3)_3$ in benzene

[Pent-1-ene] = 1·0M initially. Volume of solution = 11 ml

Reaction (A): $[RuHCl(CO)(PPh_3)_3]$ = 1·05mM; Temp. = 35 °C; *cis* : *trans* = 2·5.
Reaction (B): $[RuHCl(CO)(PPh_3)_3]$ = 0·87mM; Temp. = 80 °C; *cis* : *trans* = 0·9.
Reaction (C): $[RuHCl(CO)(PPh_3)_3]$ = 0·05mM; Temp. = 80 °C; *cis* : *trans* = 0·3.

		Extent of isomerisation	Deuterium distribution (%)						Mean deuterium number at each carbon atom [c]				
Reaction	Olefin	(%)	C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$ [a]	D.N.[b]	C1	C2	C3	C4	C5
	Pent-1-ene	0	0·4	2·6	96·8	0·2	0·0	1·97	0·97	1·00	0·00	0·00	0·00
(A)	Pent-1-ene	14	0·0	4·2	94·1	1·7	0·0	1·98	0·94	1·00	0·03	0·00	0·01
		48	0·0	10·3	85·7	3·8	0·2	1·94	1·03	0·84	0·07	0·00	0·00
	Pent-2-ene	14	0·2	5·3	83·9	9·8	0·8	2·06	1·42	0·60		0·01	0·03
		48	0·0	8·8	79·8	10·7	0·7	2·03	1·30	0·64		0·05	0·04
(B)	Pent-1-ene	12	1·0	18·3	70·7	9·9	0·1	1·90	1·06	0·76	0·00	0·08	0·00
		47	2·6	24·4	60·5	12·1	0·4	1·83	1·13	0·69	0·01	0·00	0·00
	Pent-2-ene	12	0·4	9·1	55·6	31·4	3·5	2·28	1·50	0·76		0·01	0·01
		47	0·8	13·0	53·8	28·7	3·7	2·22	1·48	0·71		0·01	0·02
(C)	Pent-1-ene	20	2·5	24·0	57·6	15·6	0·3	1·87	1·08	0·69	0·05	0·05	0·00
		38	5·6	30·4	47·1	16·6	0·3	1·76	1·11	0·61	0·01	0·03	0·00
	Pent-2-ene	20	0·6	9·2	44·1	38·7	7·4	2·43	1·58	0·80		0·01	0·04
		38	1·7	12·0	41·5	36·6	8·2	2·38	1·59	0·76		0·02	0·01

[a] More highly deuteriated pentenes not observed. [b] D.N. = deuterium number of the pentene sample. [c] Values uncertain to ±0·05.

The general features of the results in Table 2 are that intermolecular hydrogen transfer occurred in all reactions, and that each pentene tended to lose deuterium from C-2, and acquire deuterium at C-1. The ethyl group of pent-2-ene was always substantially free of deuterium, indicating that the double bond moved one position, but not two, along the hydrocarbon chain in the initial stages of reaction. These results are similar to those presented in Part IV for isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by iridium complexes in solution; indeed, in terms of both the deuterium distribution and the *cis* : *trans* ratios, reaction (C) of Table 2 of this paper is closely similar to reaction (B) of Table 2 of Part IV where a detailed discussion of mechanism is given [see especially equations (3)—(5)]. It is concluded that all reactions reported in Table 2 of this paper proceeded by an addition–abstraction mechanism involving pent-1-yl and pent-2-yl complexes as intermediates. Consequently, the decline in the *cis* : *trans* ratio with decreasing catalyst concentration was not accompanied by a change of mechanism, and is attributed to a progressive decongestion of the catalytic site brought about by a gradual increase in the degree of dissociation of phosphine ligands. Our hypothesis concerning the origins of this change in the *cis* : *trans* ratio is contained in the preceding paper.[1]

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