Homogeneous Catalysis of Olefin Isomerisation. Part III.[1] The Isomerisation of Pent-1-ene Catalysed by Solutions of Tetrakis(triethyl phosphite)-nickel(0) and of Hydridochlorocarbonyltris(triphenylphosphine)-osmium(II)

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The isomerisation of pent-1-ene to *cis*- and *trans*-pent-2-ene is catalysed at 35 °C by solutions of $Ni\{P(OEt)_3\}_4$ in benzene containing trifluoroacetic acid, and at 80 °C by solutions of $OsHCl(CO)(PPh_3)_3$ in pure benzene. The initial rate of the nickel-catalysed reaction is not diminished by the addition of triethyl phosphite, and $NiH\{P(OEt)_3\}_4{}^+$ is suggested as the catalyst. The initial rate of the osmium-catalysed reaction is retarded by the addition of triphenylphosphine, and catalyst generation is suggested to occur by dissociation of triphenylphosphine from the original complex.

The initial *cis*:*trans*-ratios in the pent-2-ene were 2·3(Ni) and 6·0(Os).

Isomerisation of [1,2-$^2H_2$]pent-1-ene has shown that, for each reaction, isotopic redistribution in the reactant is rapid, and involves only the intermolecular exchange of hydrogen and deuterium bonded to the olefinic carbon atoms. Initially, pent-2-ene contained more deuterium than the starting material; no deuterium entered the ethyl group.

The suggested mechanism involves pentyl and 1-methylbutyl intermediates. Dissociation or displacement of pent-2-ene from the catalyst occurs before the formation of 1-ethylpropyl complexes. Steric hindrance about the carbon–metal bond in 1-methylbutyl complexes is suggested in order to reconcile the conclusions (i) that the formation of 1-methylbutyl complexes from pent-1-ene is a favoured process, and (ii) that the rate of conversion of 1-methylbutyl complexes into pent-2-ene is relatively slow.

THERE are two reports in the literature of olefin isomerisation catalysed by nickel complexes in solution. Chauvin and Lefebre[2] observed that dichlorobis(pyridine)nickel(II) together with triethylaluminium in hexane catalysed but-1-ene isomerisation rapidly at 25 °C; the suggested mechanism involved π-allylic intermediates. Cramer and Lindsey[3] have reported butene isomerisation catalysed by tetrakis(triethyl phosphite)nickel(0) in acidic methanol, for which a mechanism involving alkyl intermediates was postulated. Isomerisation of undec-1-ene catalysed by diosmium noncarbonyl under the stimulus of u.v. radiation has been described.[4]

We now report isomerisation of pent-1-ene catalysed (i) by tetrakis(triethyl phosphite)nickel(0) dissolved in benzene containing trifluoroacetic acid (a modified Cramer–Lindsey system) and (ii) by hydridochlorocarbonyltris(triphenylphosphine)osmium(II) dissolved in benzene.

EXPERIMENTAL

Materials.—Tetrakis(triethyl phosphite)nickel(0)[5] and hydridochlorocarbonyltris(triphenylphosphine)osmium(II)[6] were prepared by literature methods. The nickel complex could be handled in air for short periods without decomposition. The osmium complex was stable in air. Solutions of each complex were very air-sensitive.

Benzene was dried by distillation from sodium–lead alloy (B.D.H.), stored over Linde 4A molecular sieve, and degassed on a vacuum line. Trifluoroacetic acid (B.D.H.) was distilled from silver oxide before use. Pent-1-ene and *trans*-pent-2-ene were pure as supplied; *cis*-pent-2-ene contained 5% of the *trans*-isomer but was used without purification. [1,2-$^2H_2$]pent-1-ene was prepared by the selective deuteriation of pent-1-yne catalysed by chlorotris(triphenylphosphine)rhodium(I) in 1 : 1 (v/v) benzene–phenol[7] and was purified by preparative g.l.c. The composition of the material so obtained is given in Table 1.

Procedure.—Catalytically active solutions were prepared by dissolving a known weight of complex in benzene (10 ml) which, for solutions of the nickel complex only, contained a known concentration of trifluoroacetic acid. The resulting solution was transferred to the reaction vessel previously described.[1,8] All solutions were handled under vacuum or under nitrogen. Sufficient olefin was distilled

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

[2] Y. Chauvin and G. Lefebre, *Compt. rend.*, 1964, **259**, 2105.

[3] R. Cramer and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3534.

[4] F. Asinger, B. Fell, and K. Schrage, *Chem. Ber.*, 1965, **98**, 372.

[5] R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 1964, **3**, 1062.

[6] L. Vaska, *J. Amer. Chem. Soc.*, 1964, **86**, 1942.

[7] J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, 1968, **46**, 60.

[8] B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Wells, *Discuss. Faraday Soc.*, 1968, **46**, 37.

through a column of activated alumina into a reaction vessel cooled in liquid air. The vessel was then transferred to a thermostatted tank (nickel, 35 °C; osmium, 80 °C). Liquid samples were removed through the evacuated sidearm with a syringe. For mass and ^1H n.m.r. analysis of labelled olefin, two-thirds of the solution was removed in the early stages of reaction, and the remainder after *ca.* 40% reaction.

Analyses.—Analyses were performed as described in Part II.[1]

RESULTS

Solutions of $Ni\{P(OEt)_3\}_4$ in benzene containing trifluoroacetic acid catalysed pent-1-ene isomerisation rapidly at 25 °C. Solutions of the complex were very pale yellow; the colour intensified on addition of pent-1-ene, and then diminished as isomerisation proceeded. No activity was apparent at temperatures up to 60 °C when benzene, or benzene containing acetic acid, was used as solvent.

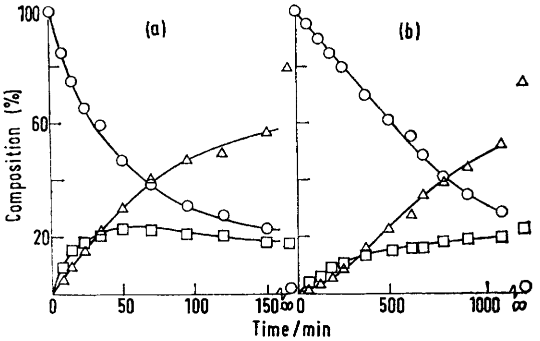

FIGURE 1 Isomerisation of pent-1-ene; variation of pentene composition with time; ○, pent-1-ene; △, *trans*-pent-2-ene; □, *cis*-pent-2-ene. [Olefin] = 1M. (a) $[Ni\{P(OEt)_3\}_4]$ = 0·5mM; $[CF_3{\cdot}CO_2H]$ = 3·5mM; *t* = 35 °C; (b) $[OsHCl(CO)(PPh_3)_3]$ = 2·0mM; *t* = 85 °C

Pale brown solutions of $OsHCl(CO)(PPh_3)_3$ in benzene catalysed pent-1-ene isomerisation slowly at 20 °C and rapidly at 80 °C.

Typical plots of composition against time are shown in Figure 1. In each system preferential formation of *cis*-pent-2-ene occurred in the early stages of reaction. However, formation of *trans*-pent-2-ene rapidly became the major process. The pentenes eventually attained the thermodynamic equilibrium composition relevant to the temperature of the experiment.

Reaction Catalysed by the Nickel Complex at 35 °C.—The initial rate of pent-1-ene isomerisation increased with increasing concentrations of complex (0·50—2·66mM) and of trifluoroacetic acid (0·21—0·70mM) but was not influenced by the addition of triethyl phosphite. Rate measurements showed poor reproducibility, possibly owing to the presence of traces of oxygen. The initial *cis* : *trans*-ratio in the pent-2-ene was *ca.* 2·3 under all conditions. The initial rate of *cis*-pent-2-ene isomerisation exceeded that of pent-1-ene isomerisation by a factor of 30 under comparable conditions; the product was mainly *trans*-pent-2-ene, and the fraction of pent-1-ene did not exceed the equilibrium value.

Although the addition of a large excess of triethyl phosphite (12—24mM) did not influence the initial rate of reaction, it caused isomerisation to stop after 40% of the pent-1-ene had reacted.

The products of the isomerisation of $[1,2\text{-}^2H_2]$pent-1-ene catalysed by the nickel complex ($[Ni\{P(OEt)_3\}_4]$ = 0·43mM, $[CF_3{\cdot}CO_2H]$ = 0·14mM, conversions = 12 and 26%) are described in Table 1. A rapid redistribution of deuterium occurred in the reactant in the early stages of reaction, and the ^1H n.m.r. spectra reveal that this involved only the hydrogen and deuterium atoms at C(1) and C(2). Pent-2-ene was formed with a higher deuterium number than the reactant, and that of the pent-1-ene decreased accordingly. No deuterium was transferred to the solvent. The ^1H n.m.r. spectra of the pent-2-ene isomers did not allow a differentiation of the hydrogen atoms bonded to C(2) and C(3); however, the splitting pattern of the resonance signal

TABLE 1

Distribution and location of deuterium in pentene (nickel-catalysed reaction)

[Pent-1-ene] = 1·0M initially. $[Ni\{P(OEt)_3\}_4]$ = 0·43mM.
$[CF_3{\cdot}CO_2H]$ = 0·14mM. Temp. = 35 °C. Volume of solution = 11 ml.

Extent of Isomerisation (%)	Deuterium distribution (%)						D.N.[b]	Mean deuterium number at each carbon atom[c]				
	C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$	$C_5H_5D_5$[a]		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
12	0·3	18·8	67·8	12·9	0·2	0·0	1·94	1·08	0·74	0·12	0·00	0·00
d	*0·5*	*17·8*	*70·3*	*11·4*	*0·0*	*0·0*	*1·93*	*0·97*	*0·96*	*0·00*	*0·00*	*0·00*
26	2·8	27·9	50·4	18·6	0·3	0·0	1·86	1·12	0·67	0·04	0·03	0·00
d	*3·5*	*31·2*	*48·4*	*16·9*	*0·0*	*0·0*	*1·79*	*0·91*	*0·88*	*0·00*	*0·00*	*0·00*
			cis-Pent-2-ene									
12	0·5	6·6	53·4	36·3	3·1	0·1	2·35					
d	*0·1*	*6·2*	*48·8*	*41·0*	*3·9*	*0·0*	*2·42*					
26	1·5	12·0	49·5	32·2	4·7	0·1	2·27	1·25	0·85	0	0·07	0·10
d	*1·1*	*15·3*	*42·9*	*33·8*	*6·9*	*0·0*	*2·30*	*1·38*	*0·92*	*0·00*	*0·00*	*0·00*
			trans-Pent-2-ene									
12	0·2	7·1	51·9	35·9	4·8	0·1	2·38					
26	0·0	11·7	47·0	34·0	6·9	0·4	2·37	1·38	0·89	0	0·10	0·00

[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 by use of p = 0·10; s = 0·82; i = 0·08.

of the hydrogen atoms bonded to C(4) indicated that there was little or no deuterium at C(3). Hence, the deuterium content attributable to the positions [C(2) + C(3)] has been allocated to C(2) in Table 1.

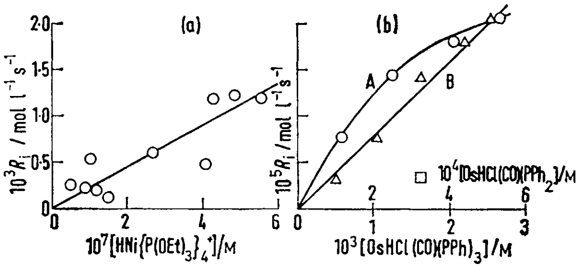

FIGURE 2 (a) Variation of initial rate of isomerisation (R_i) of pent-1-ene at 35 °C with [NiH{P(OEt)$_3$}$_4^+$]; [olefin] = 1M; (b) curve A, variation of initial rate of isomerisation (R_i) of pent-1-ene at 80 °C with [OsHCl(CO)(PPh$_3$)$_3$]; [olefin] = 1M. Squared point represents the initial rate measured in the presence of 2·0mM-PPh$_3$. Curve B, dependence of initial rate upon [OsHCl(CO)(PPh$_3$)$_2$] calculated as described in the text

Reaction Catalysed by the Osmium Complex at 80 °C.—The initial rate of pent-1-ene isomerisation increased non-linearly with increasing concentration of the complex, was severely reduced by the addition of triphenylphosphine, and was independent of olefin concentration (0·3—1·0M). Two of these features are shown in Figure 2(b). The initial *cis* : *trans*-ratio in the product was *ca.* 6·0. Isomerisation of *cis*-pent-2-ene was faster than that of pent-1-ene, initial rates being in the ratio 18 : 1. The product of pent-2-ene isomerisation was mainly *trans*-pent-2-ene; the fraction of pent-1-ene never exceeded the equilibrium value. When a 42 : 58 mixture of pent-1-ene and *cis*-pent-2-ene was admitted to the vessel, the initial rate of disappearance of each olefin was considerably reduced by the presence of the other.

TABLE 2

Distribution and location of deuterium in pentene (osmium-catalysed reaction)

[Pent-1-ene] = 1·0M initially. [OsHCl(CO)(PPh$_3$)$_3$] = 2·3mM.
Temp. = 80 °C. Volume of soution = 11 ml.

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
21	4·1	27·9	47·2	20·5	0·3	0·0	1·85					
d	*4·5*	*27·9*	*46·6*	*21·0*	*0·0*	*0·0*	*1·84*					
43	9·4	34·8	40·3	15·1	0·4	0·0	1·62	0·98	0·54	0·00	0·04	0·06
d	*11·3*	*36·6*	*38·7*	*13·4*	*0·0*	*0·0*	*1·54*	*0·97*	*0·57*	*0·00*	*0·00*	*0·00*
			cis-Pent-2-ene									
21	1·4	11·1	38·8	37·6	10·6	0·5	2·46					
d	*1·0*	*10·9*	*39·5*	*39·9*	*8·7*	*0·0*	*2·44*					
43	2·2	14·5	35·7	34·5	12·1	1·0	2·43					
			trans-Pent-2-ene									
21	0·3	9·9	36·2	38·1	14·0	1·5	2·60					
43	1·9	12·8	33·8	34·7	14·7	2·1	2·54	1·54	0·85		0·10	0·05
d	*4·0*	*19·0*	*37·4*	*30·5*	*9·1*	*0·0*	*2·22*	*1·55*	*0·67*	*0·00*	*0·00*	*0·00*

[a] More highly deuteriated pentenes not observed. [b] D.N. = deuterium number of the pentene sample. [c] Values uncertain to ±0·5. [d] Calculated distributions by use of $p = 0{\cdot}20$; $s = 0{\cdot}76$; $i = 0{\cdot}04$.

Isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by the osmium complex {[OsHCl(CO)(PPh$_3$)$_3$] = 2·3mM, conversions = 21 and 43%} is described in Table 2. Again, a rapid redistribution of deuterium in pent-1-ene was observed in the early stages of reaction, and the deuterium number of the product exceeded that of the reactant. Examination of the ^1H n.m.r. spectrum revealed that deuterium was bonded to C(3) in the pent-2-ene after 43% reaction, and hence the deuterium numbers at C(2) and C(3) cannot be resolved. Deuterium was not transferred either to the solvent or to the phosphine ligands of the complex.

DISCUSSION

Kinetics.—The positive orders in nickel complex and in trifluoroacetic acid suggest that the catalytically active species is formed by the protonation shown in equation (1). The five-co-ordinate hydride (II) has

$$\underset{(I)}{Ni\{P(OEt)_3\}_4} + CF_3{\cdot}CO_2H \rightleftharpoons \underset{(II)}{NiH\{P(OEt)_3\}_4^+} + CF_3{\cdot}CO_2^- \quad (1)$$

been characterised by Drinkard *et al.*, who reported a value of 0·3 for the equilibrium constant.[9] Figure 2(a) shows an approximately linear dependence of initial rate of pent-1-ene isomerisation upon the concentration of compound (II) calculated by use of this equilibrium constant.

The observed independence of initial rate upon the concentration of added triethyl phosphite is consistent with the generation of the active catalyst by equation (1), and confirms that dissociation of ligands from complex (II) was unimportant.* Reactions carried out

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* C. A. Tolman has informed us that *ca.* 10^{-3}M solutions of Ni{P(OEt)$_3$}$_4$ in methanol at 25 °C, acidified by *ca.* 0·1M-sulphuric acid, catalyse but-1-ene isomerisation. This reaction is of order 1·0 in HNiL$_4^+$, and of order −1·0 in P(OEt)$_3$. In this instance, dissociation of the complex clearly occurs, and HNiL$_3^+$ is suggested as the catalytically active intermediate.

[9] W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsay, jun., *Inorg. Chem.*, 1970, **9**, 392.

with added triethyl phosphite stopped after *ca.* 40% reaction for reason unknown.

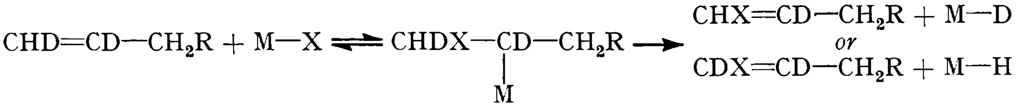
The positive fractional order in osmium complex and the inhibition by added triphenylphosphine shows that the catalytically active species in this reaction are formed by the dissociation of at least one phosphine ligand from each molecule of the original complex [equation (2)]. A linear dependence of initial rate upon

$$\underset{\text{(III)}}{\mathrm{OsHCl(CO)(PPh_3)_3}} \rightleftharpoons \underset{\text{(IV)}}{\mathrm{OsHCl(CO)(PPh_3)_2}} + \mathrm{PPh_3} \qquad (2)$$

the concentration of complex (IV) is found [see curve B of Figure 2(b)] if the equilibrium constant for the process shown in equation (2) has the value $1{\cdot}2 \times 10^{-4}$ mol l^{-1}.

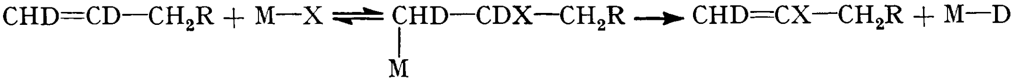
The rate constants calculated from Figure 2 are: k_{Ni} *ca.* 10^3 s^{-1} at 35 °C and $k_{\mathrm{Os}} = 4{\cdot}5 \times 10^{-2}$ s^{-1} at 80 °C. The value for the nickel-catalysed reaction is remarkably high.

Mechanism of Isomerisation.—The three main features of deuterium movement in the isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by the nickel complex are (i) intermolecular exchange of hydrogen and deuterium atoms between molecules of pent-1-ene resulting mainly in a redistribution of hydrogen and deuterium bonded to C(1) and C(2), (ii) movement of the double bond without transfer of deuterium to C(3), C(4), or C(5), and (iii) the appearance of products that are more highly deuteriated than the original reactant. Features (i) and (iii) show decisively that the reaction intermediates are pentyl complexes; participation of π-allylic intermediates would not accomplish 1,2-shift nor intermolecular transfer of deuterium. Exchange of hydrogen for deuterium and *vice versa* at C(1) may occur as shown in equation (3), and the exchange of deuterium for hydrogen at C(2) as described in equation (4) [X = H or D, R = Et]. Equation (3) results in deuterium accumulation at C(1), and according to (4) deuterium is lost from C(2). Feature (iii) listed above may occur as shown in equation (5); it is necessary to suppose that rapid dissociation or displacement of pent-2-ene from complex (VII) occurs, otherwise the eventual formation of a 1-ethylpropyl complex from (VII) would result in the appearance of deuterium in the ethyl group of pent-2-ene.



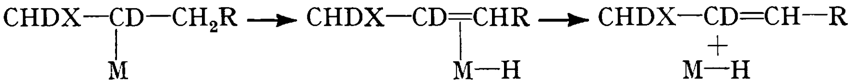
$$\mathrm{CHD{=}CD{-}CH_2R} + \mathrm{M{-}X} \rightleftharpoons \mathrm{CHDX{-}}\underset{\substack{|\\ \mathrm{M}}}{\mathrm{CD}}\mathrm{{-}CH_2R} \longrightarrow \begin{matrix}\mathrm{CHX{=}CD{-}CH_2R + M{-}D}\\ \textit{or}\\ \mathrm{CDX{=}CD{-}CH_2R + M{-}H}\end{matrix} \qquad (3)$$

(Va)

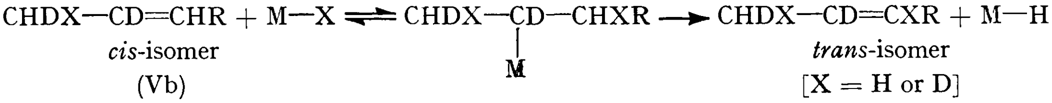


$$\mathrm{CHD{=}CD{-}CH_2R} + \mathrm{M{-}X} \rightleftharpoons \underset{\substack{|\\ \mathrm{M}}}{\mathrm{CHD}}\mathrm{{-}CDX{-}CH_2R} \longrightarrow \mathrm{CHD{=}CX{-}CH_2R + M{-}D} \qquad (4)$$

(VI)



$$\underset{\text{(Va)}}{\mathrm{CHDX{-}}\underset{\substack{|\\ \mathrm{M}}}{\mathrm{CD}}\mathrm{{-}CH_2R}} \longrightarrow \underset{\text{(VII)}}{\mathrm{CHDX{-}}\underset{\substack{|\\ \mathrm{M{-}H}}}{\mathrm{CD{=}CHR}}} \longrightarrow \underset{[\mathrm{X = H\ or\ D}]}{\mathrm{CHDX{-}CD{=}CH{-}R} \atop {+ \atop \mathrm{M{-}H}}} \qquad (5)$$



$$\underset{\substack{\textit{cis}\text{-isomer}\\ \text{(Vb)}}}{\mathrm{CHDX{-}CD{=}CHR}} + \mathrm{M{-}X} \rightleftharpoons \mathrm{CHDX{-}}\underset{\substack{|\\ \mathrm{M}}}{\mathrm{CD}}\mathrm{{-}CHXR} \longrightarrow \underset{\substack{\textit{trans}\text{-isomer}\\ [\mathrm{X = H\ or\ D}]}}{\mathrm{CHDX{-}CD{=}CXR}} + \mathrm{M{-}H} \qquad (6)$$

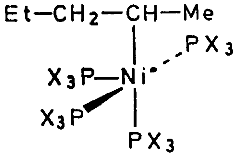
The emergence of *trans*-pent-2-ene as the major product early in the reaction, and the high activity of the nickel catalyst for the geometrical isomerisation of *cis*-pent-2-ene, shows that processes (6) and perhaps (7) may occur rapidly. Again the formation of 1-ethylpropyl complexes must be slow.

Reactions with the deuterium-labelled olefin were not analysed sufficiently late in the reaction to determine the extent of participation of (6) which results in the appearance of deuterium at C(3) in the pent-2-ene while retaining an undeuteriated ethyl group.

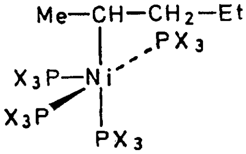
The rate of deuterium redistribution in pent-1-ene greatly exceeded that of isomerisation, showing that the pentyl ligand of the complex (Va) [see equation (3)] was more likely to revert into pent-1-ene than undergo conversion into pent-2-ene [equation (5)]. However, the rate of geometrical isomerisation of pent-2-ene exceeded that of pent-1-ene formation, showing that the pentyl ligand of complex (Vb) was more likely to become pent-2-ene than pent-1-ene. It is thus necessary to interpret the different behaviours of these complexes whose formula is apparently identical. The problem is resolved if it is supposed that there is restricted rotation

$$\text{(VII) } (\textit{cis}\text{-pent-2-ene ligand}) \longrightarrow \text{(Vb)} \longrightarrow \text{(VII) } (\textit{trans}\text{-pent-2-ene ligand}) \qquad (7)$$

about the nickel–carbon bond in (Va) and (Vb). If these intermediates have the conformations shown at the moment of their formation, and if rotation about the carbon–metal bond is slow compared with the rate of hydrogen abstraction from the 1-methylbutyl ligand, then (Va) will be converted mostly into a pent-1-ene complex and (Vb) into a pent-2-ene complex.



(Va)



(Vb)

(X = OEt)

In the isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by the osmium complex, the movements of deuterium resembled closely those observed for the nickel complex-catalysed reaction. Thus, the mechanism is adequately described above, and equations (3)—(7) apply. Positive evidence for the operation of (6) is obtained from the ^1H n.m.r. spectrum of *trans*-pent-2-ene formed after 43% conversion, which showed the presence of deuterium bonded at C(3). The presence of a little deuterium at C(4) and C(5) shows that 1-ethylpropyl intermediates were formed slowly from species (VII).

Computations.—If the probabilities of the various elementary steps are specified and if it is assumed that, after co-ordination of pent-1-ene to a catalytically active complex, the hydrocarbon entity undergoes only one reaction before being displaced by another molecule of reactant, then the distributions and locations of deuterium in the products of [1,2-$^2H_2$]pent-1-ene isomerisation can be calculated. The assumption constitutes an approximation, and requires that equation (6) can be neglected. The treatment used, which is due to Hudson,[10] defines p as the probability that pent-1-ene will undergo exchange at C(2) by the formation of a pentyl complex [equation (4)], s as the probability that pent-1-ene will undergo exchange at C(1) by the formation of a 1-methylbutyl complex [equation (3)], and i as the probability that isomerisation will occur. Tables 1 and 2 show calculated distributions and locations of deuterium together with the values of p, s, and i used. Agreement between experiment and calculation is sufficiently good for the conclusion to be firmly drawn that the probability of pent-1-ene molecules being converted into 1-methylbutyl ligands exceeded the chance of their being converted into pentyl ligands, and that the probability of isomerisation of pent-1-ene was low (Ni, 8%; Os, 4%). As suggested above, the low probability of isomerisation may arise because rotation about the carbon–metal bond in the 1-methylbutyl complex is sterically hindered.

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[10] B. Hudson, Ph.D. Thesis, University of Hull, 1971.