Homogeneous Catalysis of Olefin Isomerisation. Part I. Reactions of *trans*-[$^2H_2$]Ethylene Catalysed by Complexes of Cobalt, Ruthenium, Rhodium, and Palladium

By **B. Hudson, D. E. Webster, and P. B. Wells,*** **Department of Chemistry, The University, Hull HU6 7RX**

Reactions of *trans*-[$^2H_2$]ethylene with solutions of $CoHN_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, and of $RhH(CO)(PPh_3)_3$ in benzene at 50° have been investigated. Redistribution of hydrogen isotopes in the ethylene occurred, leading eventually to a random distribution, the reaction proceeding *via* ethyl intermediates. Solutions of the hydrido-complexes were of comparable activity, and were more active than those of $RuCl_2(PPh_3)_3$. Hydrogen exchange was observed between deuterium atoms of the olefin and protium atoms in the *ortho*-positions of the triphenylphosphine ligands of $RuHCl(PPh_3)_3$.

A solution of $PdCl_2(PhCN)_2$ in benzene at 50° catalysed the conversion of *trans*- into *cis*-[$^2H_2$]ethylene without simultaneous isotope redistribution. Routes by which this can occur are discussed.

It is now well established that a number of transition-metal complexes in solution catalyse hydrogen-transfer reactions in unsaturated hydrocarbons. In this series of papers we shall describe experimental work on one such reaction, homogeneous catalysed isomerisation (*i.e.* double-bond migration) in which complexes of all the Group VIII metals have been studied and the detailed reaction mechanisms for the different complexes are compared. Isomerisation may occur either by hydrogen atom abstraction from the olefin followed by hydrogen atom addition to the intermediate π-allylic species, or by an addition–abstraction process involving alkyl groups as intermediates. It is possible to distinguish between these alternatives when the reactant olefin is labelled deuterium, as we shall describe in later papers where pentene isomerisation is reported, but experimentation and interpretation are complex. Here we report a simple test that will distinguish between these two mechanisms. The test involves the interaction of a partially deuteriated ethylene with a solution that is catalytically active for the isomerisation of higher olefins. If the hydrogen isotopes of the partially deuteriated olefin have been redistributed in the product olefins then the formation of complexes containing ethyl ligands is confirmed, and the mechanism is one of addition–abstraction. However, ethylene is unable to form π-allylic intermediates, and hence a catalyst solution which promotes pentene isomerisation by a π-allylic mechanism will not catalyse isotope redistribution in a partially deuteriated ethylene.

We have examined the reactions of *trans*-[$^2H_2$]ethylene with solutions of five known complexes under conditions where these solutions are each active catalysts for pentene isomerisation. The mechanistic implications of this ethylene test are discussed here, and pentene isomerisation will be described in detail in subsequent papers.

The dependence of the isotopic composition of ethylene upon time (for conditions, see Experimental section)

Complex	Solvent	Reactant	$\frac{[\text{Reactant}]}{[\text{Complex}]}$	Reaction time (min)	Isotopic composition of ethylene (%) C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4	Deuterium number
		t-$C_2H_2D_2$		0	0·5	5·0	94·5	0·0	0·0	1·94
$RuCl_2(PPh_3)_3$	C_6H_6	t-$C_2H_2D_2$	80	18	0·5	6·8	90·6	2·0	0·1	1·94
				63	0·9	12·4	78·5	7·4	0·7	1·95
				360	5·5	26·0	40·9	22·7	4·9	1·95
					7·0	*26·5*	*37·4*	*23·5*	*5·5*	*1·94*
$RuHCl(PPh_3)_3$	C_6H_6	t-$C_2H_2D_2$	80	5	3·4	18·1	61·8	14·2	2·5	1·94
				12	6·4	25·7	41·5	21·7	4·7	1·93
				23	7·5	26·9	37·3	22·3	6·0	1·92
				116	8·3	28·4	37·0	21·7	4·6	1·86
$RuHCl(PPh_3)_3$	C_6D_6	t-$C_2H_2D_2$	110	23	9·1	29·1	37·0	20·6	4·2	1·82
				44	13·5	33·7	33·1	14·7	5·0	1·64
$CoHN_2(PPh_3)_3$	C_6H_6	t-$C_2H_2D_2$	79	15	7·3	26·1	37·7	23·2	5·7	1·94
$RhH(CO)PPh_3)_3$	C_6H_6	t-$C_2H_2D_2$	91	15	3·6	19·0	59·1	15·9	2·4	1·94
$PdCl_2(PhCN)_2$	C_6H_6	t-$C_2H_2D_2$	38	15	0·5	5·2	94·3	0·0	0·0	1·94

EXPERIMENTAL

Complexes.—Methods described in the literature were used for the preparations of $RuCl_2(PPh_3)_3$,[1] $RhH(CO)(PPh_3)_3$,[2,3] $CoHN_2(PPh_3)_3$,[4] and $PdCl_2(C_6H_5CN)_2$.[5] $RuHCl(PPh_3)_3$ Was prepared by stirring a mixture of $RuCl_2(PPh_3)_3$ (1 mmol) and triethylamine (20 mmol) in a benzene–ethanol (1 : 1; v/v) solvent for 1 h. The resulting purple crystals were identical with those prepared by Wilkinson's method.[6]

Hydrocarbons.—The benzene solvent was distilled from sodium in a nitrogen atmosphere, and the distillate was saturated with nitrogen before use. Since the [$^2H_6$]-benzene (Koch–Light Ltd.) contained an impurity that reacted with the $RuHCl(PPh_3)_3$, it was purified by passing it as a gas through an alumina column, and then condensing it into a flask containing $RuHCl(PPh_3)_3$. The benzene was then distilled when required into the reaction vessel attached to a vacuum-line.

trans-[$^2H_2$]Ethylene was prepared by the method of Patterson and du Vigneaud;[7] the i.r. spectrum confirmed [8] that all $C_2H_2D_2$ was present as the *trans*-isomer.

Apparatus.—The reaction vessel was identical to that described previously (vessel 3, Figure 1 of reference 9) except that the centre tube was shortened so that it no longer dipped below the surface of the catalyst solution. Vessel volumes were 30 ml when C_6H_6 was used as solvent, and 5 ml when C_6D_6 was used. Volumes of solvent employed were 4·0 ml (C_6H_6) or 0·4 ml (C_6D_6). Complex concentrations (in mmol ml^{-1}) were: 1·4(Rh), 1·6(Co), 2·5(Ru), and 3·25(Pd). Reaction vessels were placed in a thermostatically controlled bath at 50·0 ± 0·1 °C for the duration of reaction. Ethylene was removed by condensation into an attached vessel, and then analysed by mass spectrometry (A.E.I. MS 3) and, when necessary, by i.r. spectroscopy (Unicam SP 100); the relevant methods of analysis have been described elsewhere.[10] Mass spectrometric analysis of phosphines in complexes was carried out using an A.E.I. MS 902 spectrometer. ^1H N.m.r. spectra of triphenylphosphine in [$^2H_6$]benzene solution were obtained using a J.E.O.L. 100 MHz spectrometer.

RESULTS

Isotope redistribution occurred (Table 1) when *trans*-[$^2H_2$]ethylene was added at 50° to solutions of $CoHN_2(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, and $RhH(CO)(PPh_3)_3$. The cobalt and ruthenium hydrides were the most active catalysts, the rhodium hydride was of somewhat lower activity, and the dichlororuthenium complex was much less active. Isotope randomisation (Table) was achieved

---

[1] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1945.

[2] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[3] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1967, 305.

[4] J. Lorbeth, H. Nöth, and P. V. Rinze, *J. Organometallic Chem.*, 1969, **16**, P1.

[5] M. S. Kharasch, *J. Amer. Chem. Soc.*, 1938, **60**, 882.

[6] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143.

[7] W. I. Patterson and V. du Vigneaud, *J. Biol. Chem.*, 1938, **123**, 327.

[8] B. L. Crawford and R. L. Arnett, *J. Chem. Phys.*, 1950, **18**, 118.

[9] B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Wells, *Discuss. Faraday Soc.*, 1968, *No.* **46**, 37.

[10] G. C. Bond and P. B. Wells, *J. Catalysis*, 1966, **6**, 397.

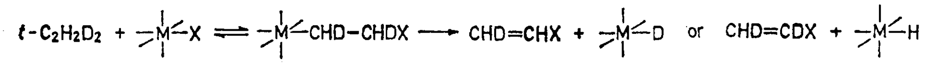
in *ca.* 15 min with the first two compounds, and in rather more than 6 h with the dichlororuthenium complex. Solutions of $PdCl_2(PhCN)_2$ did not catalyse isotope redistribution.

In reactions catalysed by solutions of $RuHCl(PPh_3)_3$ in [$^2H_0$]benzene the deuterium number of the ethylene decreased steadily as reaction proceeded, and continued to diminish after the deuterium distribution had become completely random (compare analyses after 0, 23, and 116 min). The deuterium number also decreased when [$^2H_6$]-benzene was used as solvent; analysis of triphenylphosphine after reaction by mass and n.m.r. spectrometry showed conclusively that deuterium was present at the *ortho*-positions of the phenyl groups of the phosphine, as described by others.[11,12]

Solutions of $PdCl_2(PhCN)_2$ did not catalyse the isotope redistribution reaction in ethylene (Table) but, surprisingly the i.r. spectrum of ethylene withdrawn from the vessel contained not only an absorption band at 727 cm^{-1} attributable to the vibration of *trans*-[$^2H_2$]ethylene, but also a band at 844 cm^{-1} [7] attributable to the ω_7 vibration of *cis*-[$^2H_2$]-ethylene. The asymmetric isomer of $C_2H_2D_2$ was not present, the ω_7 band at 752 cm^{-1} being absent. Further, decomposition by ethylenediamine of the palladium–olefin complex which remained in solution also provided a sample of ethylene which consisted entirely of the *trans*- and *cis*-forms of [$^2H_2$]ethylene.

DISCUSSION

Reaction of *trans*-[$^2H_2$]ethylene with a hydrido-complex may lead to the formation of ethyl ligands, and the reverse step provides a route for the formation of ethylene containing one or three deuterium atoms [see equation (1)]. This process will also enable *trans*-[$^2H_2$]-ethylene to undergo isomerisation to the *cis*-form, and analogous steps involving the product olefins will eventually cause the deuterium distribution in the ethylene to become statistically random. It then follows that the observation of such intermolecular hydrogen redistribution in ethylene is evidence for the operation of the addition–abstraction mechanism with alkyl intermediates and for the existence of hydrido-complexes in solution [equation (1)].* On the other hand, failure to observe isotope redistribution in ethylene, using a solution of a complex which is catalytically active for the isomerisation of C_4 or higher olefins, may indicate that an abstraction–addition mechanism with allylic intermediates is operative in such reactions.



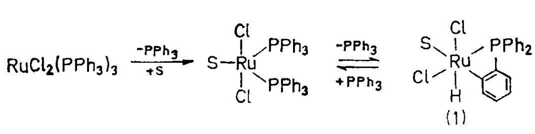
$$t\text{-}C_2H_2D_2 + {>}M{<}X \rightleftharpoons {>}M{<}CHD{-}CHDX \longrightarrow CHD{=}CHX + {>}M{<}D \text{ or } CHD{=}CDX + {>}M{<}H \qquad (1)$$

[X = H or D]

The results presented in the Table show that isotope redistribution in ethylene was catalysed by the cobalt, and rhodium complexes, and by the two complexes of ruthenium. On the basis of the discussion above, it is clear that in each case the catalytically active species is the hydrido-complex, and that ethylene molecules were in equilibrium with ethyl groups, thus this redistribution test confirms the results of other workers for these complexes.[6,11] Solutions of $RuCl_2(PPh_3)_3$ were active, showing that some of this complex was converted into a hydride in solution. A possible mechanism for its formation is discussed later.

The observation that the *ortho*-hydrogen atoms of the phosphine exchange with the deuterium from the deuteriated ethylene has been recently reported by Schunn and others [11,12] and extensively discussed by them. Where this occurs, exchange in C_2D_4 [11] is as satisfactory as redistribution in $C_2H_2D_2$ as a probe for ethyl-intermediates.

In isotope redistribution catalysed by solutions of $RuCl_2(PPh_3)_3$ (Table), it is possible that the hydrido-complex required as a catalyst was formed by a process such as equation (3), where S is a solvent molecule.† Species (1) is a hydrido-complex, having a ligand site occupied by a molecule of solvent which may be displaced by ethylene. The constant deuterium number of the olefin during the reaction (Table) with this complex shows the absence of isotope exchange in the phosphine. This presumably means that the rate of this reaction is slow when the added complex is the dichloride.

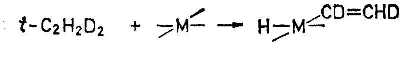


(1) (3)

Nor did we observe isotope exchange in the phosphine with $RhH(CO)(PPh_3)_3$ or with $CoHN_2(PPh_3)_3$. These observations are in disagreement with those of Schunn [11] but our reaction time may have been too short for hydrogen transfer to be detectable. It should be appreciated that redistribution in $C_2H_2D_2$ detects ethyl intermediates in the absence of simultaneous ligand-hydrogen exchange. In an earlier paper,[9] we reported that the reaction of *trans*-[$^2H_2$]ethylene with solutions of $RhCl_3(PPh_3)_3$ in chloroform solution resulted in a decrease in the deuterium number of the ethylene (from 1·96 to 1·77 during

---

* If ethylene can interact with the complex as shown in equation (2), and if either two molecules of ethylene can react at one metal centre, or if such vinylic hydride complexes can interchange hydrogen atoms, then isotope redistribution could occur. We have recently proposed this type of interaction between alkanes and platinum(II),[13] but it has not been reported for alkenes. Furthermore it appears unlikely that it will occur, as the π-electrons available in the alkene form such a strong bond to the metal.



$$t\text{-}C_2H_2D_2 + {>}M{<} \longrightarrow H{>}M{<}CD{=}CHD \qquad (2)$$

† The recently suggested alternative mode of activation of this compound,[14] by hydroperoxides is not possible under our reaction conditions.

[11] R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567.

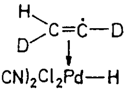
[12] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91**, 4990.

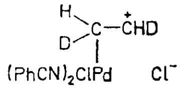
[13] R. J. Hodges, D. E. Webster, and P. B. Wells, *Chem. Comm.*, 1971, 462.

[14] J. E. Lyons, *Chem. Comm.*, 1971, 562.

110 h at 50°); this now suggests that hydrogen exchange in the phosphine was taking place.

In contrast, solutions of $PdCl_2(PhCN)_2$ with $[^2H_2]$-ethylene did not effect isotope redistribution, but *trans–cis* isomerisation occurred. The absence of redistribution confirms that co-ordination of the olefin to the metal and insertion into the metal–hydride bond followed by elimination does not take place, and so the isomerisation cannot be taking place by this route. There are two other possible types of intermediate that might be formed that will allow isomerisation without isotope redistribution. These are a free radical species (2), in which the unique carbon–hydrogen bond lies along the carbon–carbon axis and which will allow addition of the hydrogen from the metal on either side to give both *cis*- and *trans*-isomers, and a carbonium ion intermediate (3), in which rotation about the carbon–carbon single bond can occur. Intermediates somewhat analogous to (2) are proposed in the palladium-catalysed reaction of acetylene with deuterium,[15] and in the formation of *trans*-but-2-ene from but-2-yne.[16] At present we have no evidence to distinguish between these two possibilities.


(2)


(3)

We gratefully acknowledge the award of an S.R.C. studentship to B. H., and we thank Johnson Matthey and Co. Ltd., for the loan of precious metal salts. The mass spectrometers and the n.m.r. spectrometer were purchased with the aid of grants from the S.R.C.

[1/1842 *Received, 8th October,* 1971]

[15] G. C. Bond and P. B. Wells, *J. Catalysis*, 1966, **5**, 65.

[16] G. Webb and P. B. Wells, *Trans. Faraday Soc.*, 1965, **61**, 1232.