The Mechanism of Isomerization of Olefins with Transition Metal Catalysts

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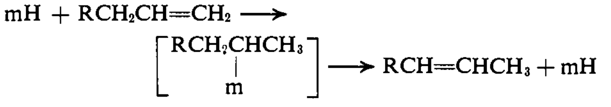
Abstract: A mechanism is proposed for the isomerization of olefins with compounds of rhodium, palladium, platinum, nickel, or iron as catalysts and with a variety of cocatalysts. A kinetically stable metal hydride with coordinated substrate olefin rearranges first to a metal alkyl, then to the metal hydride complex of the isomeric olefin. Initial hydride formation may occur by various routes depending upon the cocatalyst and the oxidation state of the metal. However, isomerization generally proceeds (and hydride is regenerated) by a reversible reaction which may be described as the reduction of proton to hydride with concurrent two-electron oxidation of the metal.

Double-bond migration, particularly in linear, terminal olefins, is catalyzed by solutions of coordination compounds of many transition metals. Frequently a cocatalyst is required; hydrogen,[1] acids,[2] and oxygenated organic compounds[3] have been used for this purpose. We recently encountered isomerization in the hydrogenation of olefins with platinum–tin chloride complexes as catalysts[4] and in the dimerization of ethylene with rhodium(I) compounds and HCl.[5] The latter system was examined more closely, and it was found that isomerization of 1-butene in CH_3OD solution led to displacement of approximately one olefin proton by deuterium for each molecule of 1-butene that was isomerized. Surprisingly, *the product contained substantial amounts of deuterated 1-butene and nondeuterated 2-butenes.*[6] In order to account for these results a variant of the hydride addition–elimination mechanism (eq 1) was proposed which incorporated a moderately stable olefin–rhodium(III) hydride. Examination of other transition metal catalysts and other cocatalysts has been undertaken to evaluate the mechanism more extensively.



$$mH + RCH_2CH{=}CH_2 \longrightarrow \left[\begin{array}{c} RCH_2CHCH_3 \\ | \\ m \end{array}\right] \longrightarrow RCH{=}CHCH_3 + mH \qquad (1)$$

Results

Compounds of rhodium(I and III), platinum(II), palladium(II), nickel(0), and iron(−II) were employed as catalysts. Recurrent characteristics of these reaction systems are that: (1) a cocatalyst is generally required; (2) regardless of the cocatalyst, isomerization is facilitated by acid; (3) isomerization in deuterated solvent yields deuterated olefin.

Rhodium-Catalyzed Isomerization. A. HCl Cocatalyst. The $((C_2H_4)_2RhCl)_2$–HCl catalyzed isomerization of butenes has been described in detail.[6] Although solutions of rhodium(I) complexes in methanolic HCl appear to be much more efficient catalysts than rhodium(III) chloride in ethanol,[3b] the two systems are potentially equivalent. Rhodium(III) chloride can be reduced by olefin[7] or ethanol[8] to rhodium(I) and, in fact, this may be essential to catalyst activity. If the rhodium trichloride–ethanol catalyst is first heated with 1-butene at 60°, the resulting solution, when freed of butene isomers and contacted with fresh 1-butene, was effective at 0°, and its activity was further increased by addition of HCl. Chloride appears to be an essential component of the catalyst. There is no detectable isomerization of 1-butene in 5 hr at 0° by a solution of bis(ethylene)rhodium(I) acetylacetonate (acacRh-$(C_2H_4)_2$) in 1 *M* ethanolic sulfuric acid.

B. Hydrogen Cocatalyst. It has been reported[1b] that 1-hexene isomerizes during its hydrogenation at 20° in the presence of rhodium trichloride. We found that rhodium(III) chloride with hydrogen as cocatalyst isomerized 1-butene more slowly than catalyst derived from $acacRh(C_2H_4)_2$ or $((C_2H_4)_2RhCl)_2$ and HCl, possibly because less rhodium is converted to a catalytically active form rather than intrinsic inferiority. (Uncertainty concerning catalyst concentration applies to most of the systems described here.) No isomerization was observed with rhodium(III) perchlorate and hydrogen.

Hydrogen will also activate a rhodium(I) compound provided that chloride (or, possibly, other halide) is present. Thus, hydrogen with $acacRh(C_2H_4)_2$ dissolved in 0.5 *M* methanolic lithium chloride isomerized 1-butene completely within 16 hr at 25,° but there was no observable reaction in the absence of lithium chloride. Rhodium(I) chloride–stannous chloride complexes[9] and hydrogen also catalyze olefin isomerization. As the Sn/Rh ratio is increased, isomerization is slower, and at 6:1 virtually stops. Isomerization in CH_3OD solution yields deuterated butenes. The isomerization/deuteration ratio is much larger when $SnCl_2$ is included with either HCl or H_2 as cocatalyst (Table I).

A base (lithium acetate, magnesium oxide, sodium bicarbonate) reduces the rate of rhodium-catalyzed

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[1] (a) G. C. Bond and M. Hellier, *Chem. Ind.* (London), 35 (1965); (b) R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 284 (1964).

[2] (a) M. Feller, H. M. Brennan, and H. S. Seelig, U. S. Patent 2,960,550 (Nov 15, 1960); (b) J. Milgrom and W. H. Urry, Abstracts, Proceedings of the Seventh International Conference on Coordination Chemistry, Stockholm, Sweden, 1962, p 264.

[3] (a) T. A. Manuel, *J. Org. Chem.*, 27, 3941 (1962); (b) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964).

[4] R. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963); *cf.* ref 1a.

[5] R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

[6] R. Cramer, *ibid.*, **88**, 2272 (1966).

[7] R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

[8] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[9] J. F. Young, R. D. Gillard, and G. Wilkinson, *ibid.*, 5176 (1964).

Table I. Composition of Butenes from Rhodium-Catalyzed Isomerization–Deuteration of 1-Butene[a]

Expt	Reactants, mmole	Butene, %	C_4H_8, %	C_4H_7D, %	$C_4H_6D_2$, %	Isom/ Deut ratio
1	$((C_2H_4)_2RhCl)_2$, 0.13	1-Butene, 59.9	77	21	2	1.3
	DCl, 1	*trans*-2-Butene, 21.2	71	25	4	
		cis-2-Butene, 18.9	63	32	5	
2	$((C_2H_4)_2RhCl)_2$, 0.13	1-Butene, 33.4	80	19	1	3
	$SnCl_2 \cdot 2H_2O$, 0.25	*trans*-2-Butene, 21.3	80	17	2	
	DC, 1	*cis*-2-Butene, 45.3	81	16	2	
3	$RhCl_3 \cdot 3H_2O$, 0.25	1-Butene, 72.4	86	13	1	1.9
	H_2, 0.25	*trans*-2-Butene, 13.7	82	16	2	
		cis-2-Butene, 13.9	86	12	2	
4	$RhCl_3 \cdot 3H_2O$, 0.25	1-Butene, 38.9	92	7	1	6
	$SnCl_2 \cdot 2H_2O$, 0.50	*trans*-2-Butene, 35.1	90	9	1	
	H_2, 0.25	*cis*-2-Butene, 26.0	90	9	1	
5	$RhCl_3 \cdot 3H_2O$, 0.25	1-Butene, 65.0 [b]				
	$SnCl_2 \cdot 2H_2O$, 0.75	*trans*-2-Butene, 16.0	99	1	0.2	35
	H_2, 0.25	*cis*-2-Butene, 19.0				

[a] All experiments at 0° with 2 ml of CH_3OD and 8 mmoles of 1-butene. [b] Mass spectroscopic analysis on unfractionated mixture of butenes.

isomerization to less than one-tenth the uninhibited rate regardless of the cocatalyst. Isomerization was not detected when 1-butene was stirred with a methanolic solution of $(py_4RhCl_2)Cl$ and $NaBH_4$ (mole ratio 1:1) for 24 hr at 0°. These reactants are reported[10] to give a rhodium hydride.

Platinum-Catalyzed Isomerizations. A. Ethanol Cocatalyst. The $((C_2H_4)PtCl_2)_2$-ethanol catalyst described by Harrod and Chalk[3b] has an induction period, and we find that isomerization is faster if the catalyst mixture is preheated for about 1 hr before exposure to olefin. Even so, the catalyst is significantly active only above about 50°.

B. Acid Cocatalyst. 1-Butene isomerized at a moderate rate at 25° (60% of 8 mmoles in 23 hr) in contact with 0.06 mmole of H_2PtCl_6, 0.31 mmole of $SnCl_2$, and 0.1 ml of CF_3COOH. Both H_2PtCl_6 and $SnCl_2$ are essential.

C. Hydrogen Cocatalyst. Isomerization of 1-pentene by platinum–tin chloride complex and hydrogen has been reported,[1a] and catalysis has been ascribed to a platinum hydride. We found isomerization to be slow in acetone or water but much faster in methanol where the rate exceeded that of CF_3COOH-cocatalyzed reactions.

Isomerization of 1-butene in CH_3OD with H_2PtCl_6–$SnCl_2$–H_2 (see Table II) resembles the rhodium-catalyzed reaction. Thus, the product contained much deuterated 1-butene and nondeuterated 2-butenes, also the deuteration/isomerization ratio was about the same at 0° as at −24°. However, in the rhodium-catalyzed reaction, isomerization exceeds deuterium exchange while with platinum there is more deuteration than isomerization. Also the ratio of *cis*- and *trans*-2-butene is significantly different. An equilibrated mixture of linear butenes contains about 22% *cis*-2-butene and 75% *trans*-2-butene at 25°. Isomerization with rhodium gives an excess of *cis*-2-butene; frequently the *cis*/*trans* ratio is greater than one. But the platinum catalyst produced more *trans*-2-butene (*cf.* Bond and Hellier[1a]).

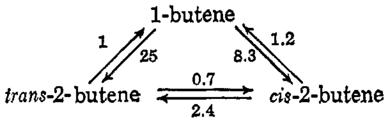
cis- and *trans*-2-butenes were isomerized with H_2PtCl_6–$SnCl_2$–H_2 in CH_3OH at 25°. The ratios of the amounts of isomeric butenes obtained from both were measured at low conversions and used to estimate the ratio of isomerization rate constants. From these ratios and rate constant ratios calculated from the composition of equilibrated linear butenes we can calculate a set of relative rate constants for platinum-catalyzed isomerization[6] (see Scheme I). The relative rate constants calculated in this way for isomerization of 1-butene to *trans*- and *cis*-2-butene are 25 and 8.3, respectively, and their ratio (3.0) corresponds to the ratio of 2-butene isomers produced from 1-butene and listed in Table II. It might also be inferred from Scheme I that interconversion of 2-butenes during isomerization of 1-butene is relatively unimportant since the rate constants are smaller than those for 2-butene formation from 1-butene. This conclusion is also substantiated in Table II because the deuterium content of the 2-butenes is nearly the same; isomerization of, say, *cis*- to *trans*-2-butene would be expected to yield more highly deuterated *trans*-2-butene.

Table II. Isomerization–Deuteration of 1-Butene with H_2PtCl_6–$SnCl_2$–H_2 in CH_3OD

	C_4H_8	C_4H_7D	$C_4H_6D_2$	$C_4H_5D_3$
A.	17 Hr at −24°[a]			
n-Butane (8.3%)				
1-Butene (71.9%)	72	27	1	<0.5
cis-2-Butene (4.5%)	55	40	5	<0.3
trans-2-Butene (15.2%)	53	41	6	<0.3
B.	7.5 Hr at 0°[b]			
n-Butane (2.0%)				
1-Butene (66.4%)	64	35	1	
cis-2-Butene (8.8%)	54	38	7	
trans-2-Butene (22.8%)	54	39	7	

[a] Isomerization, 21.5%; H–D exchange,[c] 36.0 (expressed as moles per 100 moles of butene). [b] Isomerization, 32.2%; H–D exchange,[c] 42.1 (expressed as moles per 100 moles of butene). [c] Neglecting *n*-butane.

Scheme I. Relative Rate Constants for Butene Isomerization by H_2PtCl_6–$SnCl_2$–H_2 at 25°



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(10) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

Although no isomerization was detected with H_2PtCl_6–H_2 (without $SnCl_2$) and very little with H_2PtCl_4–H_2, $((C_2H_4)PtCl_2)_2$–H_2 is a good catalyst. In contrast to the H_2PtCl_6–$SnCl_2$–H_2 system, $((C_2H_4)PtCl_2)_2$–H_2 gave more isomerization than deuteration (35.1 *vs.* 15.8%).

D. Preformed Hydride Catalyst. 1-Hexene was isomerized by *trans*-$(et_3P)_2PtHCl$ only under forcing conditions. After 22 hr at 180° about 22% was converted to 2-hexene.

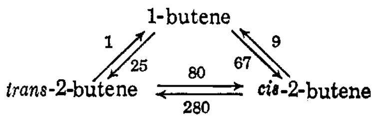
Palladium-Catalyzed Isomerization. A. Acid Cocatalyst. A comparison of isomerizations of 1-butene with Li_2PdCl_4 (Table III) shows that trifluoroacetic acid is a much better cocatalyst than a number of other oxy and oxo compounds. Its use led to 30% isomerization in 5 hr at 25°. Experiments with 1-butene and tagged trifluoroacetic acid (mole ratio 4:1) indicated that a little carboxyl hydrogen is incorporated in the isomerization product. With tritiated trifluoroacetic acid only 0.01% of the tritium was found in the butene mixture after 30% isomerization and with CF_3COOD, less than 0.3% D was transferred during 40% isomerization. Trifluoroacetic acid cocatalyzes isomerization of 1-butene by palladium(II) salicylate also.

Table III. Isomerization of 1-Butene with Li_2PdCl_4 and Cocatalysts

Cocatalyst	25° for 65 hr	50° for 8 hr, %	50° for 40 hr, %
CF_3COOH	Equilibrated	...	...
CH_3COOH	Slight	3	7
CH_3CHO	Slight	<3	1.3
$HCOOH$			4
C_6H_5COOH			6.7
$(CH_3)_3CCOOH$		<3	3
$C_2H_5OC_2H_4OH$			7.7

The Li_2PdCl_4–CF_3COOH catalyst has been used to isomerize *cis*- and *trans*-2-butenes. These are interconverted much faster than either yields 1-butene. Thus, when only 2% of *cis*-2-butene has isomerized the product contains *trans*-2-butene and 1-butene in the ratio 31:1 and under similar circumstances *trans*-2-butene yields *cis*-2-butene and 1-butene in the ratio 82:1. The relative rate constants in Scheme II were calculated[6] from these ratios and the composition of an equilibrated mixture of linear butenes.

Scheme II. Relative Rate Constants for Interconversion of Linear Butenes with Li_2PdCl_4–CF_3COOH Catalyst at 25°



It was found that platinum and palladium catalysts both convert 1-butene to *cis*- and *trans*-2-butene in the approximate ratio 1:3. The rate constants reported in Schemes I and II suggest that this result is reached by quite different routes. Platinum catalyst (Scheme I) yields 2-butenes directly in that ratio. Palladium catalyst may initially give *cis*- and *trans*-2-butene in the ratio 2.1:1 but the 2-butenes are interconverted so much more rapidly than they are formed (Scheme II) that they are detected in the ratio 1:3.

1-Butene is isomerized by Li_2PdCl_4 and aqueous acid (Table IV). Although palladium black, an established isomerization catalyst in the presence of hydrogen,[11] precipitated from some reaction mixtures, it is probably not the principal catalyst because the extent of isomerization was not proportional to the amount of palladium deposited. Isomerization increased with perchloric acid concentration but was inhibited in strong hydrochloric acid by chloride ion as shown by an equivalent effect when LiCl was substituted for part of the HCl.

Table IV. Isomerization of 1-Butene with Li_2PdCl_4 in Aqueous Acid (25° for 23 hr)[a]

Acid, *M*	Isom, %	Remarks
$HClO_4$, 0.2	<1	
$HClO_4$, 1.0	3	
$HClO_4$, 6.0	22	
HCl, 0.2	7	Complete redn of Pd^{II} to Pd^0
HCl, 1.0	25,33	Considerable redn of Pd^{II}
HCl, 7.0	None	No redn of Pd^{II}
HCl, 1.0 LiCl, 6.0	None	No redn of Pd^{II}

[a] No detectable isomerization in these acid solutions in the absence of Li_2PdCl_4.

The rate of isomerization with Li_2PdCl_4–HCl did not increase when methanol was used instead of water.

Davies[12] has examined the isomerization of 1-octene by $Na_2Pd_2Cl_6$ in acetic acid. From analysis of the infrared spectum he concluded that the olefin was not deuterated during isomerization in CH_3COOD. In essentially parallel experiments, we have isomerized 1-butene with Li_2PdCl_4 in CH_3COOD and in acetic acid with carboxyl tritium. A small but significant amount of deuterium or tritium was found in the products. About 0.5% olefin was tagged by carboxyl deuterium.

In the same publication[12] Davies describes the isomerization of $C_5H_{11}CD_2CH{=}CH_2$ and we have obtained similar results with $CH_3CD_2CH{=}CH_2$. Our dideuteriobutene was not isotopically pure; according to mass spectrometric analysis it contained 18% C_4H_8, 27% C_4H_7D, and 51% $C_4H_6D_2$, and nmr analysis showed that the deuterium was located at C_3. The composition of substrate and product butenes is shown in Table V.

Table V. Isomerization of $CH_3CD_2CH{=}CH_2$

	C_4H_8, %	C_4H_7D, %	$C_4H_6D_2$, %	$C_4H_5D_3$, %
	Substrate 1-butene, %			
Isomerized product, %	18	27	51	4
1-Butene, 70.1	12	25	56	7
trans-2-Butene, 20.9	15	43	33	9
cis-2-Butene, 9.0	14	45	32	9

Substrate 1-butene is calculated to contain 141 mole % deuterium, while the mixture of butene isomers in the product has 151 mole %. Since substrate 1-butene is

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[11] M. Dubini and F. Montini, *Chim. Ind.* (Milan), **46**, 793 (1964); G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Catalysis*, **1**, 74 (1962).

[12] N. R. Davies, *Australian J. Chem.*, **17**, 212 (1964).

the only source of deuterium, the apparent increment is attributed to analytical error.

In isomerization of $CH_3CD_2CH{=}CH_2$ to 2-butenes a deuterium–carbon bond must be broken. The results summarized in Table V indicate that the 2-butenes contain 133 mole % deuterium so most (about 90%) of the deuterium is retained in the product.

The composition of unreacted 1-butene indicates that nondeuterated 1-butene is preferentially isomerized (Table VI). Thus, although substrate 1-butene contains almost three times as much $CH_3CD_2CH{=}CH_2$ as $CH_3CH_2CH{=}CH_2$, they are consumed in nearly equal amounts.

Table VI. Isotope Effect in Isomerization of 1-Butene

	CH_3CH_2-$CH{=}CH_2$	CH_3CHD-$CH{=}CH_2$	CH_3CD_2-$CH{=}CH_2$
Mole % of substrate	18	27	51
Mole % of product	8	18	39
Mole % isomerized	10	9	12

B. Hydrogen Cocatalyst. 1-Butene was rapidly isomerized by Li_2PdCl_4 with H_2 in methanol. Reaction in acetone or water was much slower and elemental palladium always precipitated from aqueous media. Stannous chloride (Sn/Pd ratios of two or higher) prevented isomerization.

When 1-butene isomerized at −25° in CH_3OD with Li_2PdCl_4–H_2 catalyst, the products, as in other Pd-catalyzed, tagged isomerizations, contained a significant amount of deuterium (Table VII). It is seen (Table VII) that the ratio of *cis*- and *trans*-2-butenes approximates 1:3 as in platinum- (rather than rhodium-) catalyzed reactions.

Table VII. Isomerization–Deuteration of 1-Butene with Li_2PdCl_4–H_2 in CH_3OD (at −25° for 23 hr)[a]

	C_4H_8, %	C_4H_7D, %	$C_4H_6D_2$, %
n-Butane (1.8%)			
1-Butene (52.5%)	99	0.9	<0.2
cis-2-Butene (13.0%)	99	0.7	<0.1
trans-2-Butene (33.0%)	99	0.6	<0.1

[a] Isomerization, 46.8%; H–D exchange, 0.8 (expressed as moles per 100 moles of butene)

Iron-Catalyzed Isomerization. Isomerization of 1-butene with $[DFe(CO)_4]^-$ in D_2O was slower than with solutions of rhodium, platinum, or palladium compounds; the reaction was run for 5 days at 25° to get 30% conversion to 2-butenes. Results in Table VIII show that: (a) substantial amounts of deuterated 1-butene and nondeuterated 2-butene were formed; (b) the isomerization/deuteration ratio ≈ 2; (c) the *cis*-2-butene/*trans*-2-butene ratio approached 1:3.

Table VIII. Isomerization–Deuteration of 1-Butene with $(DFe(CO)_4)^-$ in D_2O (at 25° for 5 days)[a]

	C_4H_8, %	C_4H_7D, %	$C_4H_6D_2$, %
1-Butene (69.8%)	90.1	9.3	0.6
cis-2-Butene (7.9%)	80.6	18.0	1.3
trans-2-Butene (22.3%)	74.6	23.6	1.6

[a] Isomerization, 30.2%; H–D exchange, 14.9 (expressed as moles per 100 moles of butene)

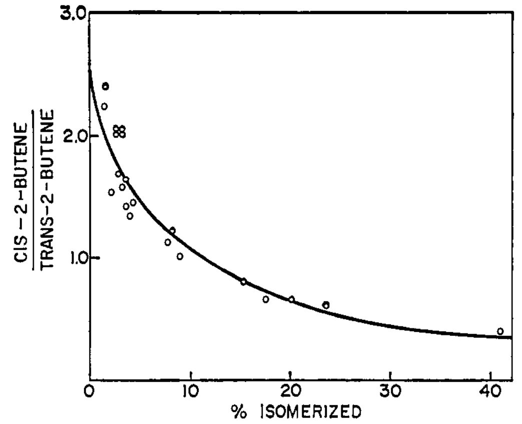


Figure 1. Product ratio from isomerization of 1-butene with nickel catalyst.

Nickel-Catalyzed Isomerization. It has been reported[13] that 1-butene is isomerized by a mixture of triethylaluminum and $NiCl_2 \cdot py_2$ and we have observed a very rapid isomerization in acidic solutions of tetrakis(triethylphosphite)nickel(0). At 25° and in 0.02 *M* methanolic H_2SO_4, 1-butene is 95% isomerized by $Ni(P(OC_2H_5)_3)_4$ within 5 min. In the absence of acid less than 3% is isomerized after 4.5 days at 25°. Isomerization in CH_3OD (Table IX) gives only a small amount of deuterated olefin. The initial ratio of *cis*-2-butene/*trans*-2-butene obtained from 1-butene (1% isomerization) is about 2.5.

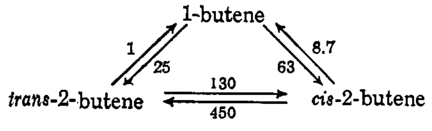
Table IX. Isomerization–Deuteration of 1-Butene with $Ni(P(OC_2H_5)_3)_4$–0.1 *M* HCl in CH_3OD (at 0° for 10 min)[a]

	C_4H_8, %	C_4H_7D, %	$CH_{72}D_2$, %
1-Butene (13.6%)	99.5	0.5	
cis-2-Butene (23.0%)	99.5	0.5	
trans-2-Butene (63.4%)	99.2	0.5	0.3

[a] Isomerization, 86.4%; H–D exchange, 0.5 (expressed as moles per 100 moles of butene).

Nickel-catalyzed isomerization of 1-butene yields *cis*- and *trans*-2-butene in ratios which extrapolate to about 2.5:1 at zero conversion (Figure 1). Isomerization of *trans*-2-butene to the extent of 4.2% gives *cis*-2-butene and 1-butene in the ratio 130:1. These ratios together with rate constant ratios calculated from the composition of equilibrated linear butenes give[6] the relative rate constants summarized in Scheme III.

Scheme III. Relative Rate Constants for Isomerization of Linear Butenes with $Ni(P(OEt)_3)_4$–H_2SO_4 at 25°



These constants indicate that isomerization of *cis*-2-butene would yield *trans*-2-butene and 1-butene in the ratio 52:1. It was found experimentally that the ratio of *trans*-2-butene to 1-butene is about 70 after 6.5%

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(13) Y. Chauvin and G. Lefebvre, *Compt. Rend.*, **259**, 2105 (1964).

isomerization of *cis*-2-butene at 25°. Since the pattern of rate constants in Scheme III is similar to that of palladium-catalyzed isomerization (Scheme II), it might be anticipated that nickel-catalyzed isomerization of 1-butene (like the palladium-catalyzed reaction) would yield *cis*- and *trans*-2-butenes in the ratio 1:3. Instead the ratio is greater than 1 until about 10% of the 1-butene has isomerized (Figure 1). Possibly nickel has a greater discrimination than palladium for coordination of 1-butene. Accordingly, little 2-butene would be coordinated to nickel and interconversion might not be important until considerable *cis*-2-butene was formed.

Exchange of D_2 with CH_3OH. Mixtures of H_2 and CH_3OD were used to study deuteration accompanying isomerizations cocatalyzed by hydrogen. As discussed later, it is believed that although molecular hydrogen can initiate isomerization, the reaction is propagated (and deuterium is introduced) by D^+ and not by D_2. Nevertheless, D_2 is available by an exchange of H_2 and CH_3OD (eq 2 and 3). This reaction, discovered by Dr. U. G. Stolberg in this laboratory, is catalyzed

$$CH_3OD + H_2 \longrightarrow CH_3OH + HD \quad (2)$$

$$CH_3OD + HD \longrightarrow CH_3OH + D_2 \quad (3)$$

by H_2PtCl_6–$SnCl_2$ and by $RhCl_3 \cdot 3H_2O$–$SnCl_2$ and is much faster than an analogous copper(II)-catalyzed[14] exchange of H_2 and D_2O. A brief kinetic study of the alternative D_2–CH_3OH exchange showed that the rate expression has the form $-d[D_2]/dt = k[D_2][Pt]$ where k has values of 0.059 l. mole^{-1} sec^{-1} and 0.85 l. mole^{-1} sec^{-1} at 0 and 25°, respectively, for the H_2PtCl_6–$SnCl_2$ catalyzed reaction. Derived values for ΔH^* and ΔS^* are 17 kcal and −3 eu, respectively. These may be compared with corresponding figures of 26 kcal and −10 eu (in water) for the copper-catalyzed H_2–D_2O exchange which has the same form for the rate expression with $k = 8.8 \times 10^{-11}$ l. mole^{-1} sec^{-1} at 0° (extrapolated from values measured at 80 to 140°).

Exchange of D_2 with CH_3OH (at 25°) was about six times as fast with 1:6 H_2PtCl_6–$SnCl_2$ as with 1:2 $RhCl_3 \cdot 3H_2O$–$SnCl_2$ at equal concentrations of transition metal salt. The exchange rate using 1:4 Li_2PdCl_4–$SnCl_2$ was about 2.5×10^{-2} of the rate with H_2PtCl_6–$SnCl_2$.

Experimental Section

The 1-butene used in this work was Matheson Co. CP grade. Vpc analysis indicated a purity of over 99% with 0.16% *cis*-2-butene and 0.12% *trans*-2-butene. 1-Hexene and *cis*- and *trans*-2-butene were Phillips pure grade. Rhodium chloride, palladium chloride, and chloroplatinic acid were purchased from Engelhard Ind. Li_2PdCl_4 was the preferred palladium catalyst because it is soluble in many organic liquids. It was prepared from stoichiometric amounts of $PdCl_2$ and LiCl in water at 80° for several hours. Water was removed from the filtered solution in a current of nitrogen and, finally, at 80° (0.5 mm) to give anhydrous Li_2PdCl_4. Tritiated water was obtained from New England Nuclear Corp., CH_3OD from Merck Sharp and Dohme of Canada, and D_2O from Columbia Chemicals Corp. Other reagents were commercial analytical reagent grade. All were used without purification.

Procedures for isomerization of 1-butene depended principally upon the cocatalyst employed. Typical experiments are described.

With Acetic Acid or Trifluoroacetic Acid Cocatalyst. A 5 × 200 mm nmr tube containing 0.01 to 0.001 g of metal salt, *e.g.*, Li_2PdCl_4, and 0.1 to 0.3 ml of acid was chilled in liquid nitrogen and evacuated, and 100 or 200 ml of 1-butene gas was added. The cold tube was sealed and brought to reaction temperature. In experiments at 25° the reactants were mixed by tumbling the tube end over end but there was no agitation of runs at 60°. The extent of isomerization was measured periodically through nmr by comparing the integrated absorptions of the methyl protons of unreacted and isomerized butenes.

In the experiments of Table III, 0.001 g of Li_2PdCl_4 and 0.2 ml of organic cocatalyst were employed.

An experiment with 0.032 g of $H_2PtCl_6 \cdot 6H_2O$, 0.093 g of $SnCl_2 \cdot 2H_2O$, 0.1 ml of CF_3COOH, and 200 ml of 1-butene resulted in 60% isomerization in 23 hr at 25°.

A mixture of 0.01 g of Li_2PdCl_4, 0.1 g of CF_3COOH, and 100 ml of 1-butene gave 7.5% isomerization in 1 hr, 20% in 3 hr, and 30% in 5 hr.

Complete isomerization occurred within 1 hr when 225 ml of 1-butene, 0.02 g of palladium(II) salicylate, and 0.1 ml of CF_3COOH were tumbled at 25°.

With Aqueous or Methanolic HCl or $HClO_4$ Cocatalyst. Glass tubes (8 × 150 mm) were charged with 0.012 g of Li_2PdCl_4 in 0.5 ml of acid solution and 200 ml of 1-butene at liquid nitrogen temperature and sealed. After reaction the product was distilled and analyzed using the integrated proton nmr spectrum. Results are entered in Table IV.

The effect of base on rhodium-catalyzed isomerizations was examined in reactors containing a magnetic stirring bar and made from a 10-ml erlenmeyer flask to the neck of which was sealed a 150 × 8 mm tube. The reactor, charged with 0.02 g of "$RhCl_3 \cdot 3H_2O$," 2 ml of ethanol, and 200 ml of 1-butene, was chilled in liquid nitrogen, evacuated, and sealed. Within 0.5 hr at 25° the olefin had equilibrated (97% isomerization). Inclusion of bases gave the following results: 0.05 g of CH_3COOLi, no isomerization in 1 hr; 0.05 g of MgO, 19% isomerization in 1 hr; 0.05 g of $NaHCO_3$, 24% isomerization in 1 hr.

With Hydrogen Cocatalyst. A reactor described in the preceding paragraph was charged with 0.25 mmole of catalyst salt and 2.00 ml of CH_3OH. It was chilled in liquid nitrogen and evacuated, and 5 ml of H_2 and 200 ml of 1-butene were added from a gas buret. The cold reactor was sealed, and it was transferred to a dewar flask containing ice–water or refluxing methyl chloride (−24°).

After reaction, the mixture of butenes was pumped from the reaction mixture (which was kept at or below the nominal reaction temperature). The butenes were analyzed by vpc. Details of the separation of butene isomers and the analysis of mixtures of deuterated butenes were described earlier.[6]

An experiment with rhodium chloride and 0.5 mmole of $SnCl_2 \cdot 2H_2O$ gave 61% isomerization in 1 hr at 0°. With 1.5 mmoles of $SnCl_2 \cdot 2H_2O$ there was no detectable isomerization in 1 hr at 0°. Without $SnCl_2$, 40% of the 1-butene was isomerized in 3 hr at 0°.

No isomerization occurred with $Rh(ClO_4)_3 \cdot 6H_2O$ (3 hr at 0°) or $(py_4RhCl_2)Cl$ (20 hr at 25°).

1-Butene was completely isomerized in 24 hr by 0.05 mmole of $acacRh(C_2H_4)_2$ in 0.5 *M* methanolic LiCl with 5 ml of H_2 cocatalyst at 25°. There was no detectable isomerization in the absence of LiCl (24 hr at 25°).

Experiments with chloroplatinic acid contained 1.5 mmoles of $SnCl_2 \cdot 2H_2O$ and led to 20% isomerization in 17 hr at −24° or 32% isomerization in 7.5 hr at 0°. For isomerization of 2-butenes at 25°, the catalyst charge was reduced to 0.06 mmole. Samples of butenes were taken at 10-min intervals for Vpc analysis until 5% of the 2-butene had isomerized (*ca.* 1 hr). In the absence of $SnCl_2$, isomerization of 1-butene by H_2PtCl_6 was not detectable after 26 hr at 0°. However, when 0.25 mmole of $((C_2H_4)PtCl_2)_2$ was used, there was 35% isomerization after 24 hr at 0°.

Isomerization with Li_2PdCl_4 and hydrogen (no $SnCl_2$) reached 47% after 23 hr at −25°.

***trans*-$(Et_3P)_2PtClH$ Catalyst.** A heavy-walled reaction tube (4 mm i.d.) was charged with 0.05 g of $(Et_3P)_2PtClH$ and 0.6 ml of 1-hexene, chilled, evacuated, and sealed. It was heated for 22 hr in a bath of refluxing *m*-dichlorobenzene (172°). The product was distilled at reduced pressure. Vpc analysis (6-ft column of 20% silicone 703 on acid-washed firebrick at 46°) indicated 77.4% of 1-hexene, and 15.8 and 6.8% of substances coming off the column after 1.7 and 3.1 min, respectively. These were identified by their infrared spectra as *trans*- and *cis*-2-hexene.

The residue left after distillation of the hexenes was identified as $(Et_3P)_2PtClH$ by its melting point and infrared spectrum. There was no detectable isomerization in experiments at 140° for 5 hr or when $(Et_3P)_2PtClH$ was omitted in controls at 172° for 22 hr.

Rhodium Chloride–Ethanol Catalyst. Heavy-walled spherical reactors (15-ml capacity) containing a magnetic stirrer and having

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[14] E. Peters and J. Halpern, *J. Phys. Chem.*, 59, 793 (1955); J. Halpern, E. R. Macgregor, and E. Peters, *ibid.*, 60, 1455 (1956).

a 20-cm neck of 8-mm tubing were charged with 0.02 g of "$RhCl_3 \cdot 3H_2O$" (0.08 mmole), 20 ml of ethanol, and 200 ml of 1-butene gas. These were sealed and heated at 60° for 20 hr. The tubes were cooled in liquid nitrogen, opened, evacuated, and warmed to 0°, and the mixture of isomerized butenes was pumped off. The reactors were chilled in liquid nitrogen and recharged with 200 ml of 1-butene and to one was added 25 ml of HCl gas. They were sealed, and the contents were stirred for 1.5 hr at 0°. The butene mixtures were distilled and analyzed by nmr. The mixture with added HCl had isomerized to the extent of 40% compared with 11% for the other.

Experiments with Tagged Carboxylic Acids. A. CH_3COOD. CH_3COOD was prepared from 0.18 ml of D_2O and 1.00 ml of $(CH_3CO)_2O$. An nmr tube containing 0.3 ml of CH_3COOD, 0.01 g of Li_2PdCl_4, and 100 ml of 1-butene was sealed and heated at 60° for 8 hr. The mixture consisted of two, clear, liquid phases with most of the palladium in the acetic acid layer. Nmr examination of the olefin fraction showed 70% isomerization and mass spectrometric analysis indicated about 0.3% C_4H_7D.

B. Carboxyl-Tritiated Acetic Acid. Tritiated acetic acid was prepared from 0.18 ml of tritiated water with an activity of 55 μcuries and 1.00 ml of acetic anhydride. A mixture of 0.3 ml of this acid, 0.01 g of Li_2PdCl_4, and 100 ml of 1-butene was heated at 60°. After 6.5 hr about 50% of the 1-butene had isomerized. The butenes were distilled, washed with 0.5 *M* aqueous NaOH, and condensed in 0.3 ml of toluene giving a solution with a volume of about 0.5 ml. This solution had an activity of 3.5×10^6 disintegrations min^{-1} ml^{-1}. The tritiated acetic acid had an activity of 14 μcuries (3.0×10^7 disintegrations min^{-1}); accordingly about 5% of the tritium was transferred to butene.

The effectiveness of the recovery technique in avoiding mechanical contamination was shown by following procedure B with isobutane instead of 1-butene. The toluene solution of recovered isobutane had an activity of 160 disintegrations ml^{-1} min^{-1}.

C. Deuterated trifluoroacetic acid was prepared by mixing 1 ml of trifluoroacetic anhydride and 0.1 ml of D_2O. An nmr tube was charged with 0.1 ml of this acid, 0.01 g of Li_2PdCl_4, and 100 ml of 1-butene, sealed, and tumbled for 20 hr at 25°. The reaction mixture was homogeneous. Analysis by vpc showed that the butenes had attained equilibrium. Mass spectrometric analysis of the separated 2-butenes indicated about 0.3% C_4H_7D in each. In a similar experiment run for 5 hr there was 38% isomerization. No deuterium was detected in the 1-butene but the *trans*-2-butene had 1% C_4H_7D.

No isomerization occurred in a blank experiment without Li_2PdCl_4, nor was any deuterium detected in the recovered 1-butene.

D. Tritiated trifluoroacetic acid was prepared from 1.00 ml of trifluoroacetic anhydride and 0.1 ml of the tritiated water described in B. An nmr tube containing 0.1 ml of tritiated trifluoroacetic acid, 0.01 g of Li_2PdCl_4, and 100 ml of 1-butene was sealed and tumbled for 5 hr at 25° (to give about 30% isomerization). The mixture of butenes was recovered as in B. The toluene solution had an activity of 4×10^3 counts min^{-1} ml^{-1}. Since the activity of the trifluoroacetic acid was calculated to be about 10^7 counts min^{-1}, 0.02% of the tritium was incorporated in the butenes.

Experiments with $CH_3CD_2CH{=}CH_2$. Synthesis of the hydrocarbon has been described.[6] An nmr tube was charged with 0.016 g of Li_2PdCl_4, 0.1 ml CF_3COOH, and 200 ml of "$CH_3CD_2CH{=}CH_2$," chilled in liquid nitrogen, evacuated, sealed, and tumbled at 25° for 24 hr. The isomerized hydrocarbon was recovered, analyzed, and separated by vpc for mass spectrometric analysis.[6]

Stabilization of $Li_2PdCl_4H_2$ with 1-Butene. Four nmr tubes were each charged with 0.5 ml of 0.05 *M* Li_2PdCl_4 in acetone, 100 ml of 1-butene gas, and 1 ml of H_2. Another group of four tubes was similarly charged except that 0.5 ml of liquid *n*-hexane was used instead of 1-butene. Within 65 hr all the Pd^{II} in the tubes containing *n*-hexane was reduced to elemental Pd, while the solutions in tubes containing 1-butene remained homogeneous.

Stabilization of Platinum Catalyst with 1-Hexene. Four nmr tubes were charged with 0.75 ml of 1-hexene and 0.25 ml of a benzene solution which was 0.003 *M* in $((C_2H_4)PtCl_2)_2$ and 0.7 *M* in C_2H_5OH. A second set of four tubes was similarly charged except that 0.75 ml of cyclohexane was used instead of 1-hexene. The tubes were sealed and heated at 100° for 2 hr. A platinum mirror covered the walls of all the tubes containing cyclohexane, while the reaction mixture in the tubes containing 1-hexene remained clear and homogeneous.

Isomerization of 2-Methyl-1-pentene. A tube containing 0.005 g of $acacRh(C_2H_4)_2$, 0.5 ml of 2-methyl-1-pentene, and 0.1 ml of 2 *M* HCl in methanol was chilled in liquid nitrogen, evacuated, sealed, and tumbled at 25° for 20 hr. The hydrocarbon layer was separated and subjected to vpc analysis. It contained 85% of unreacted 2-methyl-1-pentene and 15% of another substance which was identified as 2-methyl-2-pentene from its infrared spectrum.

Isomerization–Deuteration with $(DFe(CO)_4)^-$ in D_2O. The catalyst solution was prepared by adding 1.6 ml of $Fe(CO)_5$ (12 mmoles) to a solution of NaOD prepared from 0.51 g of Na (22 mmoles) and 10 ml of D_2O.[15] This mixture was stirred at 25° for 24 hr and gave a deep red solution calculated to contain about 0.7 mmole of $(DFe(CO)_4)^-$ per ml. A 2.0-ml portion was transferred by hypodermic syringe to an evacuated reactor chilled with liquid nitrogen, and 200 ml of 1-butene gas was added. The mixture was stirred at 25° for 5 days and deuterated, and isomerized butenes were recovered and analyzed as described earlier.

Rate of CH_3OH–D_2 Exchange. This reaction was studied in creased, round-bottom flasks fitted with a stirrer consisting of a shaft of tantalum (pivoted in dimples at the top and bottom of the flask) to which were tied several laces of polytetrafluoroethylene. The stirrer, driven at 1300 rpm through a magnet sealed to the top of the shaft, whipped much of the reaction solution into a spray. The flask was immersed in a bath maintained within 0.2° of the nominal temperature and charged with catalyst dissolved in CH_3OH, flushed twice with D_2, then pressured to 1 atm with D_2. Samples of gas (5 ml) were withdrawn periodically and analyzed for H_2, HD, and D_2 by mass spectroscopy.

Dependence of rate on the concentration of hydrogen was calculated by plotting log per cent H_2 in the gas samples against time. In experiments using 20.00 ml of solution containing 0.25 mmole of H_2PtCl_6 and 1.5 mmoles of $SnCl_2$ the points lay on straight lines (15% D_2 left at last observation) with slopes of 7.2×10^{-5} sec^{-1} (at 25.0) and 3.9×10^{-6} sec^{-1} (at 0.0°). These rates are arbitrary since the gas phase is a reservoir of H_2 and the rate depends on the volume of this reservoir. To calculate an intrinsic rate, the arbitrary rate was divided by the fraction of H_2 in the liquid phase, *viz.*, the volume of solution times the solubility of H_2 in methanol divided by the volume of gas phase of the reactor.[16] The intrinsic values of *k* (for solutions which are 0.0125 *M* in Pt) are $k_{0°} = 7.39 \times 10^{-4}$ sec^{-1} and $k_{25°} = 1.06 \times 10^{-2}$ sec^{-1}.

Dependence of the rate of CH_3OH–D_2 exchange on [Pt] was measured as follows. The reaction flask was charged with 20.00 ml of methanol, 0.002 mmole of H_2PtCl_6, 0.012 mmole of $SnCl_2 \cdot 2H_2O$, and D_2 at 1 atm as described above. After 1 hr the partially exchanged gas mixture was withdrawn for H_2, HD, and D_2 analysis. The reaction mixture was then blanketed with nitrogen and enough concentrated H_2PtCl_6 and $SnCl_2$ solution added to bring the amounts in the rector to 0.008 and 0.048 mmole, respectively. This solution was stirred with D_2 for 1 hr and the product was collected for analysis. Similar runs were made with 0.016, 0.032, and 0.063 mmole of H_2PtCl_6 together with 0.096, 0.192, and 0.38 mmole of $SnCl_2 \cdot 2H_2O$, respectively. Values for arbitrary rate constants for each platinum concentration were calculated from the expression (2.000 − log % H_2 after 1 hr)/3600. These values for *k* were plotted against [Pt] and, since they fall on a straight line, the rate is proportional to the platinum concentration (with an invariant Pt/Sn ratio of 1/6).

Since rate is proportional to the platinum concentration, values for *k* (for the expression rate = $k[D_2][Pt]$) are $k_{0°} = 0.059$ l. $mole^{-1}$ sec^{-1} and $k_{25°} = 0.85$ $mole^{-1}$ sec^{-1}. Using these values and the specific rate at 25° it is calculated that $k = 4.1 \times 10^{12} \exp(17{,}300/RT)$.

Discussion

The mechanism recently proposed[6] to describe isomerization of olefins with rhodium(I)–HCl catalyst is also applicable to catalysis by other transition metals. This mechanism comprises addition of metal hydride to coordinated olefin followed by an isomerizing elimination. The experiments reported here indicate that transition metal compounds become catalysts for isomerization only when they are converted to hydrides. Thus, isomerization of 1-butene is not observed at

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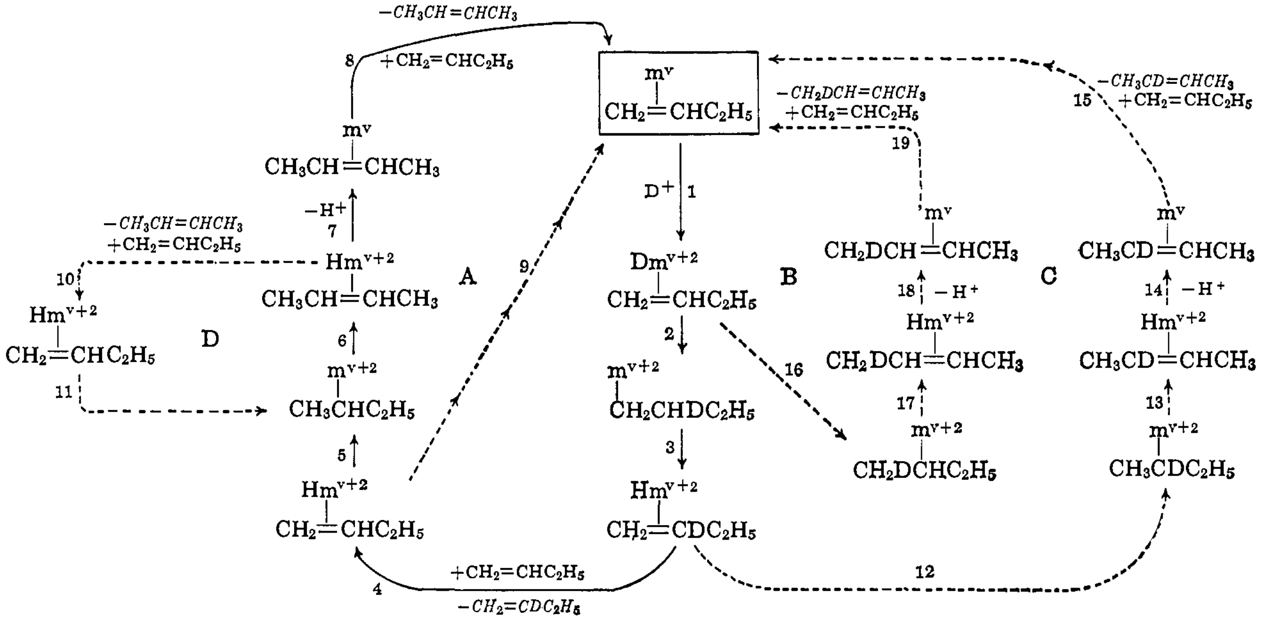
[15] H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **79**, 6116 (1957).

[16] G. Just, *Z. Physik. Chem.*, **37**, 342 (1901), reports that $l_{25°} = 0.09449$ ml of H_2/ml of solution and $l_{20°} = 0.09016$ ml/ml. Extrapolation of these values by plotting log *l* *vs.* T^{-1} (A. Lannung, *J. Am. Chem. Soc.*, **52**, 68 (1930)) gave a value $l_{0°} = 0.0733$. For these calculations we assumed $l_{25°} = 0.0945$, $l_{0°} = 0.0733$.

Scheme IV. Isomerization–Deuteration of 1-Butene (Products Are in Italic; Minor Reactions Are Shown by Dotted Arrows)



25° with any of the following: $Ni(P(OC_2H_5)_3)_4$, $((C_2H_4)_2Rh^ICl)_2$, H_2PtCl_6–$SnCl_2$, Li_2PdCl_4, or (at 0°) $RhCl_3$. However, the first four are activated by acid and the last four by hydrogen. It has been established[5,17] that hydrides are formed under just these conditions.

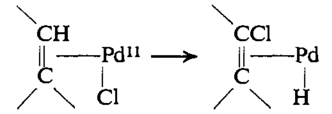
A variety of hydride-generating reactions is available. Cocatalysts may produce hydride by oxidation of a carbon compound (eq 4), disproportionation of hydrogen (eq 5), oxidation of a metal with hydrogen (eq 6) or proton (eq 7), or displacement of hydrogen from coordinated olefin (eq 8). Although any of these furnishes *initiating* hydride, the exchange of olefin protium and solvent deuterium, which accompanies isomerization in CH_3OD or CH_3COOD, indicates that hydride is regenerated from solvent proton; accordingly, the *working* cocatalyst is proton. (This is confirmed by the inhibiting effect of added base.) Reversible oxidation of transition metal by solvent proton (eq 7) serves as the means of exchanging olefinic hydrogen with solvent proton.

$$CH_3CH_2OH + OH^- + Clpt^{II} \longrightarrow CH_3CHO + Hpt^{II} + Cl^- + H_2O \quad (4)$$

$$H_2 + Clrh^{III} \longrightarrow Hrh^{III} + Cl^- + H^+ \quad (5)$$

$$H_2 + rh^I \longrightarrow H_2rh^{III} \quad (6)$$

$$HCl + rh^I \longrightarrow Hrh^{III}Cl \quad (7)$$


(8)

Isomerization proceeds by three reversible reactions (eq 9–11): (a) oxidation of a metal–olefin complex by proton; (b) olefin exchange; and (c) hydride addition to complexed olefin to give a metal alkyl. The over-all reaction is a complicated function of the relative rates of these steps as influenced by the structure of the coordinated olefin, the metal, and its auxiliary ligands. The isomerization–deuteration of 1-butene is illustrated in Scheme IV.

$$\begin{matrix} m^v \\ | \\ \text{olefin} \end{matrix} + H^+ \rightleftarrows \begin{matrix} Hm^{v+2} \\ | \\ \text{olefin} \end{matrix} \quad (9)$$

$$\begin{matrix} m^{v \text{ or } v+2} \\ | \\ \text{olefin} \end{matrix} + \text{olefin}' \rightleftarrows \begin{matrix} m^{v \text{ or } v+2} \\ | \\ \text{olefin}' \end{matrix} + \text{olefin} \quad (10)$$

$$\begin{matrix} Hm^{v+2} \\ | \\ \text{olefin} \end{matrix} \rightleftarrows \begin{matrix} m^{v+2} \\ | \\ \text{alkyl} \end{matrix} \quad (11)$$

A surprising consequence of isomerization of 1-butene in CH_3OD is that it yields deuterated 1-butene and nondeuterated 2-butene. This can occur through cycle A of Scheme IV. Deuteration of $m^v(CH_2{=}CHC_2H_5)$ leads (eq 1, 2, and 3, Scheme IV) *via* $m^{v+2}CH_2CHDC_2H_5$ to $Hm^{v+2}(CH_2{=}CDC_2H_5)$. *Deuterated* 1-butene is displaced from $Hm^{v+2}(CH_2{=}CDC_2H_5)$ by 1-butene, eq 4, giving $Hm^{v+2}(CH_2{=}CHC_2H_5)$ as the other product. $Hm^{v+2}(CH_2{=}CHC_2H_5)$ continues to undergo hydride addition and elimination at the olefinic bond. Usually hydrogen adds to C_2, but this is a trivial step since elimination can only regenerate the initial complex. Occasionally addition of hydride to C_1 will occur (eq 5) and if this is succeeded by elimination of hydrogen from C_3 (eq 6), a m^{v+2} complex of 2-butene will be formed. Reduction by loss of H^+ gives a m^v complex of 2-butene (eq 7) from which nondeuterated 2-butene is displaced by 1-butene (eq 8), completing the reaction cycle. This reaction path produces deuterated 1-butene and nondeuterated 2-butene in the one-to-one ratio which is approximated by many rhodium catalyst systems.[6] Maintenance of a one-to-one ratio requires that the hydride complex of 2-butene, $Hm^{v+2}(CH_3CH{=}CHCH_3)$, is reduced to $m^v(CH_3CH{=}CHCH_3)$ (by loss of a proton) without undergoing olefin exchange while the corresponding 1-butene complex, $Hm^{v+2}(CH_2{=}CHC_2H_5)$, is not reduced but, instead, undergoes a hydride addition (eq 5) that leads to isomerization. This difference could be explained by slower displacement of coordinated 2-butene or by greater stability of rhodium(III)

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(17) (a) A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964); (b) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962); (c) R. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, 87, 658 (1965); (d) L. Vaska and J. W. Di Luzio, *ibid.*, 84, 679 (1962).

hydride when coordinated to 1-butene. If 2-butene were displaced from $Hm^{v+2}(CH_3CH{=}CHCH_3)$ by 1-butene (eq 10) then reaction cycle D (Scheme IV) would intervene and isomerization would exceed deuteration. If, on the other hand, $Hm^{v+2}(CH_2{=}CHC_2H_5)$ were reduced to $m^{v}(CH_2{=}CHC_2H_5)$ (eq 9), deuteration would occur without isomerization. Both situations have been encountered experimentally and can reasonably be related to the rate of olefin exchange.

Deuterated 2-butenes are obtained through cycles B and C of Scheme IV. If $Hm^{v+2}(CH_2{=}CDC_2H_5)$ undergoes readdition of hydride to C_1 (eq 12) rather than displacement of $CH_2{=}CDC_2H_5$ by $CH_2{=}CHC_2H_5$, further reaction (eq 13, 14, and 15) will yield $CH_3CD{=}CHCH_3$. This occurs about one-quarter of the time in a rhodium(I)–HCl catalyst system.[6] If deuterium in $Dm^{v+2}(CH_2{=}CHC_2H_5)$ adds to C_1, the isomeric deuteriobutene, $CH_2DCH{=}CHCH_3$, results (eq 16–19). This happens about one-fifteenth of the time with the rhodium catalyst.[6]

It is not proposed that reaction is limited to the steps in Scheme IV. Analogs of these reactions occur which involve isomerized or deuterated butene or which are trivial because there is no ultimate structure change. For example, coordinated 1-butene in the olefin hydride produced by eq 4 might be displaced by another 1-butene molecule but that would be a trivial reaction. Hydride addition to give a nondeuterated *n*-butyl complex, $m^{v+2}CH_2CH_2C_2H_5$, also occurs, but this can only regenerate the original hydride. The only meaningful reactions are 5 or 9.

Rhodium Catalyst Systems. Isomerization of 1-butene with $acacRh(C_2H_4)_2$–HCl has been discussed elsewhere.[6] Since the isomerization/deuteration ratio approximates 1/1 between -25 and 0° over a wide range of conversions, it is probable that reactions 9 and 10 of Scheme IV occur infrequently.

Although H_2 activates both rhodium(I) and rhodium(III) compounds, HCl is a cocatalyst only for rhodium(I) complexes. The active systems can produce rhodium(III) hydride (eq 5–7), but HCl and a rhodium(III) compound cannot. No isomerization was observed in the absence of chloride; thus neither $acacRh^{I}(C_2H_4)_2$–H_2 nor $Rh^{III}(ClO_4)_3 \cdot 6H_2O$–$H_2$ was active. Similarly, Harrod and Chalk[3b] found rhodium heptanoate inactive, and although Rinehart and Fuest[18] isomerized *trans*-2-butene with alcoholic rhodium nitrate, the rate is slow enough (0.4% after 1 hr at unspecified temperature) to indicate a qualitative difference from chloride-containing mixtures. Earlier work on rhodium-catalyzed ethylene dimerization[5] suggests that halide is involved in both hydride formation and addition to coordinated olefin.

A methanol solution of $[py_4Rh^{III}HCl]Cl$ does not perceptibly isomerize 1-butene. One explanation is that olefin will not displace pyridine to give an olefin–hydride complex. Another possibility is that initial isomerization occurs but not enough proton is available in the alkaline solution to regenerate rhodium(III) hydride from rhodium(I).

Coordination of olefin to platinum(II) is accelerated by $SnCl_2$.[4] If the isomerization/deuteration ratio is controlled by the rate of olefin exchange and if $SnCl_2$ accelerates exchange of olefin on rhodium, it would be expected that addition of $SnCl_2$ to the rhodium catalyst system would favor eq 10 as compared to eq 7 (Scheme IV) thus accounting for the increased isomerization/deuteration ratio (Table I). Gross increments of $SnCl_2$ inhibit isomerization probably by blocking the coordination of olefin. The relative amounts of *cis*- and *trans*-2-butene may vary with the auxiliary ligands, but the data of Table I do not reveal a consistent pattern.

An objection has been raised to stepwise migration of the double bond in the rhodium chloride catalyzed conversion of 1,3-cyclooctadiene to the 1,5 isomer because the 1,4 isomer was not detected in the reaction mixture.[19] However, since 1,4-cyclooctadiene does not form a stable rhodium(I) complex, its concentration cannot exceed the amount required for equilibrium with 1,3-cyclooctadiene. No publication giving the equilibrium ratio has been found, but it is reported[20] that 1,3-cyclooctadiene is more stable than the 1,5 isomer by 4.7 kcal. Accordingly, the concentration of 1,4-cyclooctadiene (with stability closer to 1,5-hexadiene) might be so low that its detection would be difficult. It is pertinent that Nicholson and Shaw[21] found that an excess of 1,5-cyclooctadiene was isomerized to a mixture of 1,3 and 1,4 isomers in the preparation of $(RhCl(C_8H_{12}))_2$ from "$RhCl_3 \cdot 3H_2O$" and 1,5-cyclooctadiene.

Palladium Catalyst Systems. Much current research on isomerization with transition metals involves palladium catalysis, and many observations have been reported concerning a variety of olefins. Most results are explicable in terms of the hydride addition–elimination mechanism. Although some solvent proton is incorporated in the olefin during isomerization it is much less than with other metals except nickel.[22] This is attributed to faster olefin exchange of palladium compounds[23] which leads, by repetition of cycle D of Scheme IV, to isomerization with little deuteration.

The probable oxidation states are Pd^0 and Pd^{II}. Although elemental palladium precipitated from some isomerization systems,[3b] complexes of Pd^0 are stabilized by appropriate coordination,[24] and we found that solutions of Li_2PdCl_4 in acetone to which hydrogen is added remain homogeneous if they contain 1-butene. A similar effect of ethylene or propene on mixtures of $((C_2H_4)PtCl_2)_2$ and H_2 was reported by Flynn and Hulbert.[25] The potential required to oxidize Pd^{II} to Pd^{IV} is so high that hydride formation according to eq 12 is unlikely.

$$pd^{II} + H^+ \longrightarrow pd^{IV}H \qquad (12)$$

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(18) *Chem. Eng. News*, **43** (6), 40 (1965).

(19) R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, **86**, 2516 (1964).

(20) R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, 40, 175 (1963).

(21) J. K. Nicholson and B. L. Shaw, *Tetrahedron Letters*, No. 39, 3533 (1965).

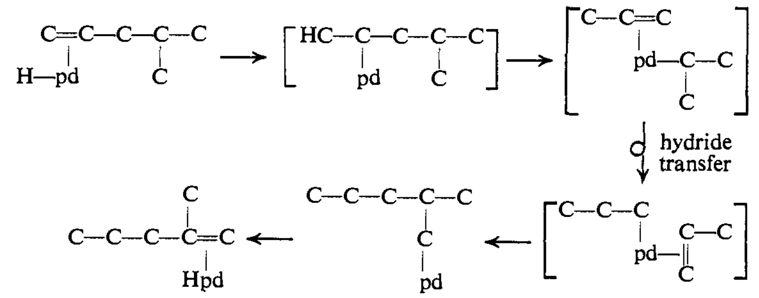
(22) Hydrogenations catalyzed heterogeneously by palladium are notable for minimal exchange of elemental hydrogen and olefinic proton; *cf.* G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 132 (1964).

(23) It has been inferred that the rate of coordination of ethylene to palladium is mass transfer controlled: P. M. Henry, *J Am. Chem. Soc.*, **86**, 3246 (1964). The corresponding platinum complex, which has comparably great thermodynamic stability, requires hours for its formation.

(24) A. B. Fasman, G. G. Kutyukov, and D. V. Sokol'skii, *Dokl. Akad. Nauk SSSR, Phys. Chem. Sect.*, **158**, 958 (1964).

(25) J. H. Flynn and H. M. Hulburt, *J. Am. Chem. Soc.*, **76**, 3393, 3396 (1954).

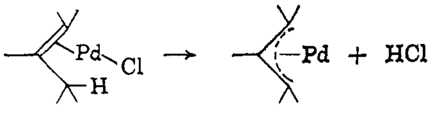
Scheme V. Isomerization of 4-Methyl-2-pentene

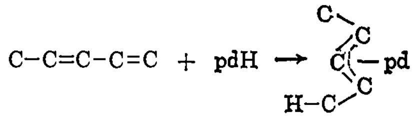


We have obtained experimental evidence to support Harrod and Chalk's proposal[3b] that palladium hydride may be formed by eq 8. After 24 hr at 25° a reaction mixture comprising 6 mmoles of *cis*-2-butene, 1 mmole of C_2D_4, 0.1 ml of CF_3COOH, and 0.01 g of Li_2PdCl_4 yields a mixture of butenes (14% isomerization) which is 0.6% deuterated. Further, vpc analysis of the gaseous product discloses a trace component which appears to be vinyl chloride. Apparently deuteride, which is formed by exchange between C_2D_2 and $(PdCl_4)^-$ (eq 8), is subsequently incorporated in butene.

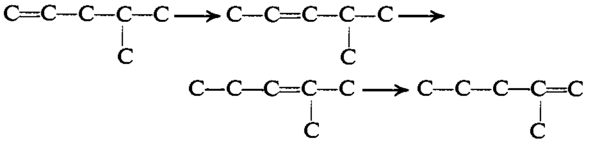
Several earlier observations are explicable on the basis of initiation by olefin hydrogen. For example, *cis*-2-pentene isomerizes more slowly than 1-pentene ($PdCl_2 \cdot 2C_6H_5CN$ catalyst) with a short induction period which is eliminated by addition of 5% 1-pentene.[26] A possible interpretation, namely, that internal olefins provide hydride more slowly than terminal olefins, is supported by the observation that synthesis of aldehydes or ketones by oxidation of olefins with palladium chloride is slower for internal than for terminal olefins.[27] This oxidation has been interpreted as involving a metal hydride formed by displacement of olefin hydrogen by hydroxyl.

Palladium catalysts may be deactivated by conversion to π-allyl complexes.[28] The life of the catalyst is related to the ease with which the substrate olefin or its isomer(s) is converted to a π-allyl compound. Thus, of a group of four hexenes, the one with most branching at olefin carbons deactivates palladium catalyst most rapidly.[29] Branched olefins are most easily converted to π-allyl complexes[30] as shown by eq 13. Also, it was reported[26] that 1,4-pentadiene did not isomerize under conditions appropriate for 1-pentene. However, the trace of conjugated diene produced by a little isomerization would be expected to deactivate a hydride catalyst through formation of a π-allyl complex according to eq 14.

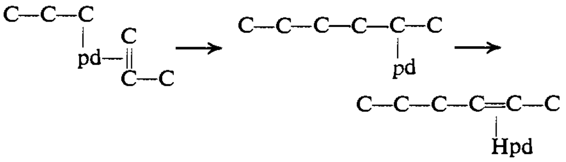

(13)


(14)

A serious objection to stepwise isomerization by addition and elimination of hydride was raised by Sparke, Turner, and Wenham[29] who observed that during isomerization of 4-methyl-1-pentene, the ratio 2-methyl-1-pentene/2-methyl-2-pentene exceeds the equilibrium ratio. This could not occur if isomerization followed eq 15. It is suggested that part of the 2-methyl-1-pentene is formed by a palladium-catalyzed cleavage of 4-methyl-1-pentene into two propylene units which recombine to give the terminal olefin (Scheme V).[31] It is reported that propylene is dimerized to linear and branched hexenes by rhodium(III) chloride,[32] and that palladium chloride catalyzes olefin dimerization.[33] Sparke, *et al.*,[29] find linear hexenes in their isomerization products and although this may occur as an impurity in substrate 4-methyl-1-pentene, it could also arise through eq 16.


(15)

$$C{=}C{-}C{-}\underset{\textstyle C}{C}{-}C \longrightarrow C{-}C{=}C{-}\underset{\textstyle C}{C}{-}C \longrightarrow C{-}C{-}C{=}\underset{\textstyle C}{C}{-}C \longrightarrow C{-}C{-}C{-}\underset{\textstyle C}{C}{=}C \quad (15)$$


(16)

Palladium-catalyzed isomerizations are especially susceptible to inhibition by competing ligands such as Cl^- or $SnCl_3^-$. Competition with acetic acid may explain the observation that $(C_6H_5CN)_2PdCl_2$ isomerized neat 2-methyl-1-pentene,[29] but $Na_2Pd_2Cl_6$ does not isomerize the same olefin in acetic acid.[12] Selective coordination would also account for the discovery[24] that 1-hexene inhibits isomerization of 4-methyl-1-pentene.

In the isomerization of $CH_3CD_2CH{=}CH_2$, most of the deuterium is retained in the 2-butene which, according to nmr absorption, is principally $CH_3CD{=}CDCH_3$. If the results summarized in Table VI are taken to correspond to a deuterium isotope effect (k_H/k_D) of ≈2, formation of $CH_3CD{=}CDCH_3$ is best

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[26] G. C. Bond and M. Hellier, *J. Catalysis*, **4**, 1 (1965).

[27] J. Smidt, *Angew. Chem.*, **71**, 176 (1959).

[28] J. F. Harrod and A. J. Chalk, *Nature*, **205**, 280 (1964).

[29] M. B. Sparke, L. Turner, and A. J. M. Wenham, *J. Catalysis*, **4**, 332 (1965).

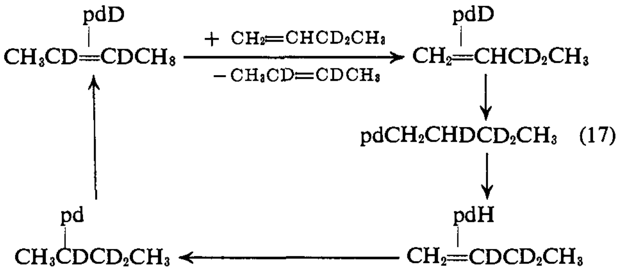
[30] R. Hüttel and H. Christ, *Chem. Ber.*, **97**, 1439 (1964).

[31] This explanation was suggested by a related rearrangement discovered by Professor Roy Miller, while he was associated with the Elastomers Department of the Du Pont Co. He is currently studying other aspects of the reaction at the University of North Dakota. Our attempts to provide evidence for a palladium-catalyzed cleavage of 4-methyl-1-pentene by isomerizing it in the presence of ethylene and isolating a pentene have not succeeded.

[32] T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 6538 (1965).

[33] J. Smidt, W. Hafner, and J. Sedlmeier, German Patent 1,193,934 (1965).

interpreted in terms of an intermolecular deuterium transfer (eq 17).[34]



(17)

Platinum isomerization catalysts containing $((C_2H_4)PtCl_2)_2$,[28] $((C_2H_4)PtCl_2)_2$–acid,[2b] $((C_2H_4)PtCl_2)_2$–alcohol,[3b] $((C_2H_4)PtCl_2)_2$–silanes,[35] $(PtCl_4)^{2-}$–$SnCl_2$–H_2,[1a] and H_2PtCl_6[2b] have been described by other investigators. The range of catalysts suggests that analogs of any of eq 4–8 may initiate reaction, but inhibition of isomerization in basic systems[2b] indicates that a reaction such as eq 18 is principally involved in hydride synthesis.

$$\mathrm{pt^{v}} + \mathrm{H^+} \longrightarrow \mathrm{Hpt^{v+2}} \qquad (18)$$

Both $Pt^0 \rightleftarrows Pt^{II}$ (like palladium) and $Pt^{II} \rightleftarrows Pt^{IV}$ ($d^8 \rightleftarrows d^6$, like rhodium) are plausible oxidation states for platinum in isomerization systems. Related reactions are summarized in eq 19 ($X = Cl^-$ or NO_3^-; $L = ph_3P$).[36]

$$Pt^0L_3 \underset{KOH}{\overset{HX}{\rightleftarrows}} (Pt^{II}HL_3)X \underset{+L}{\overset{-L}{\rightleftarrows}} (PtHXL_2) \qquad (19)$$

and eq 20.[17b] Falk and Halpern[37] have described the acid-catalyzed H–D exchange of $HPt^{II}Cl(et_3P)_2$ with D_2O in terms of eq 20.

$$HPt^{II}Cl(et_3P)_2 + HCl \longrightarrow H_2Pt^{IV}Cl_2(et_3P)_2 \qquad (20)$$

Although platinum salts are inferior to those of palladium for oxidation of olefins, Harrod and Chalk's results[3b] indicate that platinum hydride may be formed from olefin by an analog of eq 8. They report that isomerization of 1-hexene is autocatalytic and that isomerization of internally unsaturated linear hexenes is catalyzed by 1-hexene. This would correspond to participation of a platinum(II) hydride and oxidation numbers 0 and 2 for platinum in the isomerization reaction.

Isomerization proceeds at lower temperatures with hydrogen cocatalyst. Hydrogen reacts with platinum–tin chloride complexes[17c] to give a hydride, $(HPt(SnCl_3)_4)^{3-}$, presumably of platinum(II), thus suggesting platinum(0) and platinum(II) intermediates in isomerization. Hydrogen is also an effective cocatalyst with $((C_2H_4)PtCl_2)_2$. In this case formation of a platinum(II) hydride and HCl (analog of eq 5) or a platinum(IV) dihydride (analog of eq 6) is conceivable, giving no clue to the oxidation states during isomerization.

It is expected that activation of a platinum(II) complex with acid will give a platinum(IV) hydride (*cf.* eq 7). However, with CF_3COOH–H_2PtCl_6–$SnCl_2$ catalyst, tin (II), and not platinum(II), may be oxidized by proton to give platinum(II) hydride. Other workers who studied acid cocatalysis[2b] worked at 100° and may have produced hydride by olefin oxidation (analog of eq 8) rather than by oxidation of platinum(II) to a platinum(IV) hydride.

Isomerization of 1-butene in CH_3OD with H_2PtCl_4–$SnCl_2$–H_2 catalyst leads to excessive deuteration (Table II). This would be expected if exchange of olefin on platinum were slow compared to rhodium or palladium, because (a) reaction cycle A of Scheme IV would be shortcut by eq 9 and (b) reaction cycle C would be favored relative to cycle A. Increased participation of cycle C is indicated by deuteration of about 40% of the 2-butene in the platinum system (Table II) as compared with 25% with rhodium catalyst (Table I) and 20% with iron catalyst (Table IV).

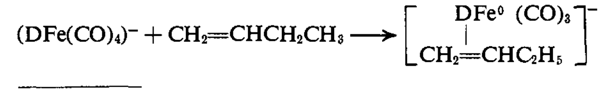
Although $SnCl_2$ accelerates olefin coordination, it also competes for a coordination site,[4] and olefin exchange of platinum(II) may be faster in the absence of $SnCl_2$ after an olefin ligand has been coordinated.[38] With a platinum catalyst derived from $((C_2H_4)_2PtCl_2)_2$ and H_2 there was more isomerization (35 mole %) than deuteration (17 mole %).

There is less than 1% isomerization of 1-butene (25°/22 hr) with H_2PtCl_4–H_2 in the absence of $SnCl_2$. Possibly coordination of olefin to platinum is prohibitively slow in the absence of an activating ligand such as $SnCl_3^-$ or ethylene, but other steps in isomerization may be affected critically. Thus, addition of ethylene to the platinum hydride, $HPtCl(et_3P)_2$ (eq 21), requires 95° and 80 atm[17b] but we have found that in the presence of 1 mole % $SnCl_2$ (based on platinum hydride) equilibrium (K = 35 l. mole^{-1}) is attained within 0.5 hr at

$$HPtCl(et_3P)_2 + C_2H_4 \rightleftarrows C_2H_5PtCl(et_3P)_2 \qquad (21)$$

25° and 1 atm. The presence of $SnCl_2$ also appears to affect the ratio of *cis*- and *trans*-2-olefins formed when a terminal olefin is isomerized. Like Bond and Hellier,[1a] we got relatively more *trans* isomer in the presence of $SnCl_2$ than Harrod and Chalk[3b] in its absence. A similar effect was noted in rhodium-catalyzed isomerizations.

Iron-Catalyzed Isomerization. It is interesting that isomerization of 1-butene by $(DFe(CO)_4)^-$ in D_2O follows a pattern of H–D exchange similar to the rhodium- and platinum-catalyzed reactions. Referring to Scheme IV, the low valence state, m^v, would be Fe(–II). Olefin complex of Fe(0) would first be formed by displacement of CO[39] (eq 22) and further reaction Scheme IV would yield isomerized and deuterated olefins and



$$(DFe(CO)_4)^- + CH_2{=}CHCH_2CH_3 \longrightarrow \left[\begin{array}{c} DFe^0\ (CO)_3 \\ | \\ CH_2{=}CHC_2H_5 \end{array}\right]^- \qquad (22)$$

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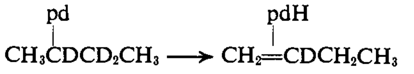
[34] We are indebted to a referee for suggesting this route to $CH_3CD{=}CDCH_3$. Scattering of deuterium to the terminal carbon atoms, which could ensue from the reaction



$$\underset{CH_3CDCD_2CH_3}{\overset{pd}{|}} \longrightarrow \underset{CH_2{=}CDCH_2CH_3}{\overset{pdH}{|}}$$

appears not to be important. This is consistent with the rate constants summarized in Scheme II which suggest that hydride is eliminated from C_3 much faster than from C_1.

[35] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965). These authors showed that some of the effective silanes will convert $((R_3P)_2PtCl_2)$ to hydride. On the basis of reported results, those silanes which give persistently active catalyst solutions may be rather tenuously classified as those likely to give acidic reaction mixtures.

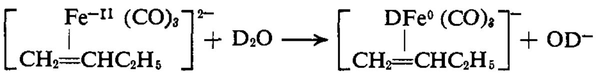
[36] F. Cariati, R. Ugo, and F. Bonati, *Chem. Ind.* (London), 1714 (1964).

[37] C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, **87**, 3524 (1965). It is interesting that this exchange has a strong dependence on the concentration of chloride ion.

[38] R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

[39] F. Basolo, A. T. Brault, and A. J. Poë, *J. Chem. Soc.*, 676 (1964).

an olefin complex of Fe(−II) which could be oxidized[40] by D_2O (eq 23).

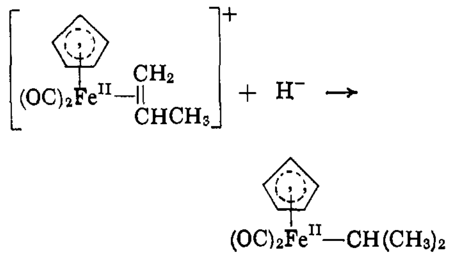


$$\left[\overset{\text{Fe}^{-\text{II}}(\text{CO})_3}{\text{CH}_2{=}\text{CHC}_2\text{H}_5}\right]^{2-} + \text{D}_2\text{O} \longrightarrow \left[\overset{\text{DFe}^{0}(\text{CO})_3}{\text{CH}_2{=}\text{CHC}_2\text{H}_5}\right]^{-} + \text{OD}^- \quad (23)$$

Isomerizations catalyzed by iron carbonyls have already been explained in terms of an iron carbonyl-hydride catalyst.[3a] In support it is noted that isomerization mixtures have the characteristic red color of iron carbonyl anion and that pyridine, which converts $Fe(CO)_5$ into $(Fe^{-II}(CO)_4)$,[41] is an especially effective cocatalyst.

The product from iron catalysis has an isomerization/deuteration ratio of 2/1 and 20% of the 2-butene is deuterated indicating that olefin exchange is fast relative to loss of proton. There is about three times as much *trans*- as *cis*-2-butene.

Green and Nagy found[42] that coordinated propene in $[\pi\text{-}C_5H_5Fe(CO)_2(C_3H_6)]^+$ reacts with $NaBH_4$ to give an isopropyl (not *n*-propyl) complex (eq 24). Consequently it might be proposed that in isomerization, hydride addition would give an isobutyl iron alkyl and therefore much deuterated 2-butene. However, only 20% of the 2-butene is deuterated; two explanations are offered. (a) Hydride addition to olefin coordinated to Fe^0 gives a primary alkyl rather than a secondary alkyl, in contrast to Fe^{II}. (b) Insertion of an olefin in an iron hydride gives a primary alkyl whereas bimolecular reaction of an iron–olefin compound with noncoordinated hydride gives a secondary alkyl.

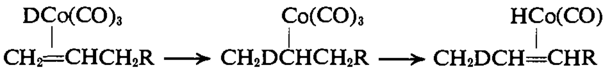


(24)

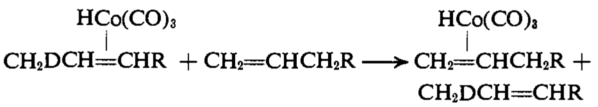
Nickel-Catalyzed Isomerization. Isomerization of 1-butene with $Ni(P(OC_2H_5)_3)_4$ and acid is consistent with Scheme IV. The oxidation numbers involved are Ni^0 and Ni^{II}. Nickel and palladium are similar in three respects: (a) the amount of deuteration accompanying isomerization is quite low, (b) neither catalyst requires an activating ligand such as halide (needed with rhodium) or $SnCl_3^-$ (with platinum), and (C) interconversion of 2-butenes is very fast.

Cobalt-Catalyzed Isomerization. Roos and Orchin[43] have reported recently that isomerization of allylbenzene with $DCo(CO)_4$ in hexane solution gives propenylbenzene of which only about 5% is deuterated. They also noted no isotope effect when rates using $HCo(CO)_4$ and $DCo(CO)_4$ were compared. These results appear to be consistent with the hydride addition–elimination mechanism described by Heck and Breslow.[44] The rate-determining step would be dissociative (S_N1) displacement of CO by olefin (eq 25) and consequently there is no isotope effect. After about 20 isomerization cycles (eq 26 and 27), only the first of which would yield deuterated propenylbenzene, cobalt hydride is destroyed by oxidation or reduction of cobalt (depending upon whether cobalt hydride is regarded as protonic or hydridic) and cannot be regenerated in this system.

$$\text{DCo(CO)}_4 + \text{CH}_2{=}\text{CHCH}_2\text{R} \longrightarrow \text{DCo(CO)}_3(\text{CH}_2{=}\text{CHCH}_2\text{R}) + \text{CO} \quad (25)$$



$$\overset{\text{DCo(CO)}_3}{\text{CH}_2{=}\text{CHCH}_2\text{R}} \longrightarrow \overset{\text{Co(CO)}_3}{\text{CH}_2\text{DCHCH}_2\text{R}} \longrightarrow \overset{\text{HCo(CO)}_3}{\text{CH}_2\text{DCH}{=}\text{CHR}} \quad (26)$$



$$\overset{\text{HCo(CO)}_3}{\text{CH}_2\text{DCH}{=}\text{CHR}} + \text{CH}_2{=}\text{CHCH}_2\text{R} \longrightarrow \overset{\text{HCo(CO)}_3}{\text{CH}_2{=}\text{CHCH}_2\text{R}} + \text{CH}_2\text{DCH}{=}\text{CHR} \quad (27)$$

Acknowledgments. The vpc technique was designed and analyses were made by Mrs. Adah B. Richmond. Mr. W. M. Kipp and Mrs. Nancy Hillyard carried out the mass spectroscopic analyses and calculations.

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[40] Description of transition metal hydrides as compounds of H^- may be merely a convenient formalism in the case of analogs of $(HFe(CO)_4)^-$, which give a proton on ionizing ($K = 10^{-13.4}$): P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, 71, 3035 (1949). If it is assumed that $(HFe(CO)_4)^-$ is a compound of Fe(−II) then there is no valence change in isomerization–deuteration with this catalyst but D^+ exchange with solvent is slow in comparison with olefin exchange.

[41] W. Hieber and R. Werner, *Chem. Ber.*, 90, 286 (1957).

[42] M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1, 58 (1963).

[43] L. Roos and M. Orchin, *J. Am. Chem. Soc.*, 87, 5502 (1965).

[44] R. F. Heck and D. S. Breslow, *ibid.*, 83, 4023 (1961).