Organic and Biological Chemistry

Olefin Coordination Compounds of Rhodium. IV. The Mechanisms of the Synthesis of 1,4-Hexadiene from Ethylene and Butadiene and of Its Isomerization to 2,4-Hexadiene

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Abstract: The rhodium-catalyzed reaction of ethylene–butadiene mixtures yields hexadienes almost exclusively rather than a dimer of either olefin. This selectivity appears to be the consequence of thermodynamic control through a relatively stable π-crotylrhodium(III) compound with coordinated ethylene. The catalyst is a rhodium alkyl which is generated *in situ* through (1) reduction of rhodium(III) to rhodium(I) by olefin followed by (2) protonation and olefin insertion. It appears that after the rhodium(III) alkyl is formed, the oxidation number of rhodium is invariant during hexadiene synthesis; this is in contrast to rhodium-catalyzed olefin isomerization and ethylene dimerization which include a reversible oxidation of rhodium(I) by HCl in every reaction cycle. Isomerization of 1,4-hexadiene resembles monoolefin isomerization but is retarded because the catalyst is sequestered by the product conjugated diene.

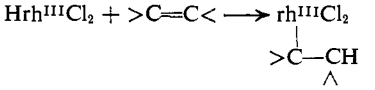
Ethylene and butadiene combine under mild conditions in the presence of rhodium(III) chloride to give 1,4-hexadiene[1] in 90% yields and high conversions. This specificity for an alkylation product containing both olefins is unexpected since the same catalyst converts ethylene to butenes at about the same rate under similar conditions. Consequently, the reaction has been studied in some detail to find an explanation.[2] Reaction occurs at ambient or higher temperature and pressure in the presence of about 0.1% "rhodium trichloride trihydrate." For example, a mixture of 3.1 moles of C_4H_6, 2.7 moles of C_2H_4, 0.2 g of "$RhCl_3 \cdot 3H_2O$," and 1 ml of ethanol undergoes 54% conversion after 16 hr at 50° in a 400-ml silver-lined autoclave and yields a mixture of 2% butenes, 91% C_6 diene (of which 20% is conjugated diene), 3% C_8 diene, and 4% higher olefin. With excess ethylene, further reaction of hexadienes gives chiefly C_8 diolefins. Formation of higher dienes and isomerization to conjugated dienes are both favored by higher temperatures. Except for trace products, the structures of the oligomers correspond to 1,4 addition of a vinyl group and hydrogen to a conjugated olefin. With 1,3 dienes, hydrogen becomes attached to C_1 and the vinyl group to C_4.

Discussion

Structure of the Rhodium Catalyst. Although "$RhCl_3 \cdot 3H_2O$" catalyzes olefin addition reactions (ethylene to ethylene or ethylene to butadiene), it is not immediately effective. There is an induction period, especially apparent at lower temperatures, during which it is converted to an active form. The chemistry of the activation of rhodium trichloride has been described in detail in an earlier paper.[3] It consists of reduction of rhodium(III) to rhodium(I) (eq 1),[4] oxidation of rhodium(I) by proton, especially HCl, to a rhodium(III) hydride (eq 2), and reaction of this hydride with coordinated olefin to give a rhodium(III) alkyl (eq 3).

$$\mathrm{Rh^{III}Cl_3 \cdot 3H_2O + C_2H_4 \longrightarrow rh^{I}Cl + 2HCl + CH_3CHO + 2H_2O} \qquad (1)$$

$$\mathrm{rh^{I}Cl + HCl \longrightarrow Hrh^{III}Cl_2} \qquad (2)$$



$$\mathrm{Hrh^{III}Cl_2 + {>}C{=}C{<} \longrightarrow \underset{\displaystyle \overset{|}{>C-\underset{\wedge}{C}H}}{rh^{III}Cl_2}} \qquad (3)$$

With a solution of a rhodium(I) compound and HCl in methanol the induction period is eliminated. Bis(ethylene)chloridorhodium(I),[5] $[(C_2H_4)_2RhCl]_2$, or bis(ethylene)acetylacetonatorhodium(I),[6] $acacRh(C_2H_4)_2$, are suitable sources of rhodium(I). These react with HCl[7] to yield the ion $[C_2H_5Rh^{III}Cl_3s_2]^-$ from which ethylene may be displaced by an excess of butadiene to give the stable π-crotylrhodium(III) complex (**1**) (eq 4).

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(1) T. Alderson, U. S. Patent 3,013,066 (1961); T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

(2) Similar condensations of ethylene and butadiene are catalyzed by iron(III) acetylacetonate with triethylaluminum (G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964)), or compounds of nickel or cobalt (D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem., Intern. Ed. Engl.*, **4**, 327 (1965); B. S. Friedman, U. S. Patent 2,599,249 (1952); T. J. Kealy, French Patent 1,388,305 (1964); British Patent 1,015,867 (1965)).

(3) R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

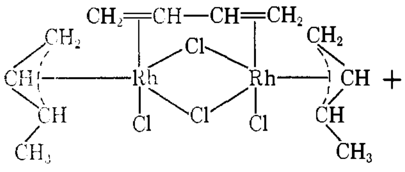
(4) In this and subsequent equations, the symbol "rh" is used for rhodium when ligands are omitted from a formula either for the sake of clarity or uncertainty concerning the exact structure. It is believed that rhodium(III) is hexacoordinate and that the omitted ligands are either Cl^- or solvent.

(5) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(6) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(7) s represents a solvent molecule. As discussed in ref 3, this is a clean reaction below about −15°. Ethylene dissociates reversibly from the initial product, $[C_2H_5Rh^{III}(C_2H_4)Cl_3s]^-$, and may be pumped off at that temperature. Increasingly above 10°, the insertion of coordinated ethylene, leading to n-$C_4H_9Rh^{III}Cl_3s_2$, becomes a significant source of impurity. Nevertheless, the dissociation and evolution of ethylene are so much faster than insertion that solutions of $[C_2H_5Rh^{III}Cl_3s_2]^-$ suitable for many purposes can be made by reaction of aqueous or methanolic HCl with one of the ethylene complexes of rhodium(I) at 25°.

$$2[C_2H_5Rh^{III}Cl_3s_2]^- + 3C_4H_6 \longrightarrow$$



$$+ 2Cl^- + 2C_2H_4 \quad (4)$$

1

The proposed formula of **1** is based upon elemental analysis and the following properties. (1) The infrared spectrum has absorptions (at 1450, 1429, 1373, 1197, and 1029 cm^{-1}) which are characteristic of π-crotyl complexes.[8] (2) The nmr spectrum is consistent with coordinated π-crotyl and butadiene ligands (see Experimental Section). (3) The low dipole moment (2.63 D.) indicates a substantial cancellation of bond moments. (4) The amount of ethylene released in the reaction of butadiene with $[C_2H_5Rh^{III}Cl_3s_2]^-$ corresponds to complete elimination of C_2 units. (5) In the hydrogenation of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ with PtO_2 catalyst, 7 moles of hydrogen is absorbed, metallic rhodium precipitates, and butane is liberated as shown in eq 5. (6) Ammonia or triphenylphosphine displaces only 1 mole of butadiene indicating that only one of the three C_4 units is butadiene. (7) Reaction with hot, concentrated, aqueous HCl yielded about 1 mole of gas (50–60% 1-butene, 15–20% 2-butene, and 5–25% butadiene) and a liquid product consisting of about 85% 2-chlorobutane and 15% 1-chloro-2-butene.[9] Reaction with 10% KOH in ethylene glycol at 60° liberated *trans*-2-butene.

$$(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6) + 7H_2 \longrightarrow 2Rh + 4HCl + 3C_4H_{10} \quad (5)$$

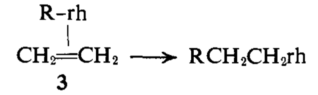
Compound **1** has been described by Powell and Shaw who prepared it from rhodium(III) chloride and butadiene.[10] Similar properties are attributed to other π-allylic derivatives of rhodium(III).

Although $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ is only sparingly soluble in methanol, it dissolves rapidly when a methanol suspension is exposed to ethylene. About 2.4 equiv of ethylene is absorbed, and then reaction virtually stops. Glpc analysis of the reaction solution indicated that 1,4- and 2,4-hexadienes had been formed. Some details of the reaction are summarized in Figure 1 which is interpreted as follows. During period A (first 12 min) coordinated butadiene was displaced by ethylene (eq 6) giving a methanol-soluble complex (**2**). Just at the end of that time, $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ was all dissolved. Period B is believed to correspond to conversion of butadiene (both $\pi\text{-}C_4H_7$ and C_4H_6, released according to eq 6) into hexadienes. This merges after about 50 min into period C, when higher oligomers are formed.

$$(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6) + 2C_2H_4 + 2Cl^- \longrightarrow 2[\pi\text{-}C_4H_7RhCl_3(C_2H_4)]^- + C_4H_6 \quad (6)$$

2

Basis of Discrimination for Addition of Ethylene to Butadiene. The chemistry of ethylene dimerization[3] and of π-methallyl complexes of rhodium[10] suggests an explanation for the selective addition of ethylene to butadiene. The rate-determining step in dimerization of ethylene is insertion of an olefin (ethylene) between rhodium and an alkyl (ethyl) group[3] (eq 7). A system

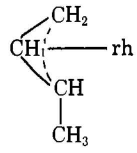


$$\overset{\text{R-rh}}{\overset{|}{CH_2{=}CH_2}} \longrightarrow RCH_2CH_2rh \quad (7)$$

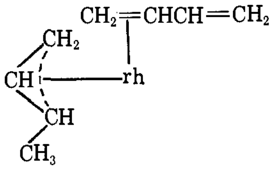
3

containing a mixture of olefins might be expected to contain complexes with a variety of alkyl and olefin ligands corresponding to the olefins in the mixture. If, to a first approximation, the slow insertion reactions of these complexes proceed at about the same rate, the composition of the product will be determined primarily by the relative concentration of the alkylolefin complexes which are analogs of **3** rather than by the different rate constants for insertion. It is suggested that *preferential formation of 1,4-hexadiene is a consequence of the relatively high stability of* **4** (*eq 9*). A high concentration of **4** is indicated because, first, it is expected that equilibrium in eq 8 will be shifted to the

$$C_4H_6 + C_2H_5rh \rightleftharpoons$$

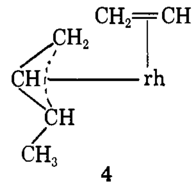


$$+ C_2H_4 \quad (8)$$



$$+$$

$$C_2H_4 \rightleftharpoons$$



$$+ C_4H_6 \quad (9)$$

4

right as a consequence of the greater stability of π-allyl complexes compared with σ-alkyls, and, secondly, data summarized in Figure 1 indicate that ethylene readily displaces coordinated butadiene; *i.e.*, the equilibrium is shifted to the right in eq 9.

Kinetics of the Addition of Ethylene to Butadiene. The rate of dimerization of ethylene is describable[3] in terms of eq 10. Addition of ethylene to butadiene is

$$-d[C_2H_4]/dt = k[C_2H_4][H^+][Cl^-][Rh] \quad (10)$$

also first order in ethylene, proton, chloride,[11] and rhodium when the rate is restricted by low concentration of one of these species. But, in addition, the rate varies with the butadiene concentration. The concentra-

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[8] E. O. Fischer and H. Werner, *Z. Chem.*, 2, 174 (1962).

[9] Reaction of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ with HCl might be expected to yield primarily butadiene and linear butenes. Addition of hydrogen chloride to these olefins would give chlorobutenes and 2-chlorobutane. Possibly there is a preliminary rearrangement of the π-crotyl group to σ-crotyl. Cleavage of σ-crotyl complexes has been shown to yield 1-butene: P. D. Sleezer, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 85, 1890 (1963); J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), 3, 421 (1965).

[10] (a) J. Powell and B. L. Shaw, *Chem. Commun.*, 323 (1966); (b) G. Paiaro, A. Musco, and G. Diana, *J. Organometal. Chem.* (Amsterdam), 4, 466 (1965); J. Powell and B. L. Shaw, *Chem. Commun.*, 236 (1966).

[11] Hexadienes are not formed in the absence of halide, which parallels the behavior of rhodium catalysts in 1-butene synthesis.[3] Exposure of a mixture of ethylene and butadiene to a solution of $acacRh(C_2H_4)_2$ in ethanolic H_2SO_4 yields polybutadiene. It is also significant that $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ does not catalyze hexadiene synthesis. Reaction of this complex with HCl and butadiene yields $(\pi\text{-}C_4H_7)(\pi\text{-}C_5H_5)RhCl$. Coordination of ethylene for hexadiene synthesis would presumably give a chloride-free, nonreactive ion $[(\pi\text{-}C_4H_7)(\pi\text{-}C_5H_5)Rh(C_2H_4)]^+$.

tions of H^+, Cl^-, and Rh do not change during reaction and, accordingly, the reaction might be expected to follow second-order kinetics. In fact, the order of the rate dependency on butadiene concentration depends on the temperature (first order at 50° and a fractional order at 30°; see Figure 2) so it was found advantageous to treat the data in terms of modified first-order kinetics.

Table I lists, in column 2, the slopes of first-order rate curves for the first 15% of reaction at 50° and over a threefold range of butadiene concentration. It is apparent that these are proportional to the butadiene concentration (column 3, Table I) as expected for first-order dependence on butadiene concentration. On the other hand, at 30°, the rate is approximately proportional to $[C_4H_6]^{0.34}$ (column 3, Table II).

Table I. Effect of Butadiene Concentration on the Rate of Addition of Ethylene to Butadiene at 50°

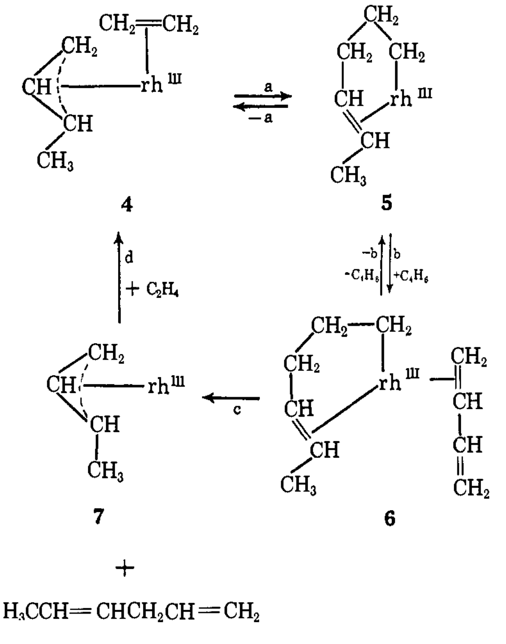
$[C_4H_6]$, arbitrary units	d ln $(P - P_\infty)$/ dt × 10^5, sec^{-1}	Slope/ $[C_4H_6]$ × 10^5
1	5.48, 5.18	5.48, 5.18
2	10.3, 10.2	5.15, 5.10
3	15.7, 15.9	5.23, 5.30

Table II. Effect of Butadiene Concentration on the Rate of Addition of Ethylene to Butadiene at 30°

$[C_4H_6]$, arbitrary units	d ln $(P - P_\infty)$/ dt × 10^5, sec^{-1}	Slope/ $[C_4H_6]^{0.34}$ × 10^5
1	4.56, 4.03	4.56, 4.03
2	5.62, 5.83	4.42, 4.56
4	7.14, 6.50	4.42, 4.03
8	9.28, 8.82	4.45, 4.31

To explain these kinetics *it is proposed that at 50° the rate-determining step is release of 1,4-hexadiene* (step c, Scheme I) *rather than olefin insertion.* As compared with the product of ethylene insertion which is formed in ethylene dimerization,[3] **5** is stabilized by its chelate structure.[12] A study of rhodium-catalyzed olefin isomerization[13] indicates that hydrogen transfer in **6** (step c, Scheme I) from the hexenyl ligand to coordinated butadiene would be a fast reaction. Slow release of 1,4-hexadiene is therefore attributed to low concentration of **6**,[14] which is proportional to the concentration of butadiene.

Scheme I. Synthesis of 1,4-Hexadiene by the Rhodium-Catalyzed Addition of Ethylene to Butadiene



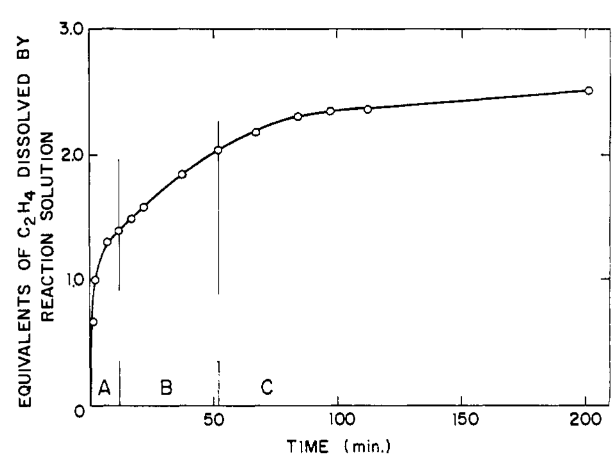


Figure 1. Absorption of ethylene by a suspension of 0.35 g of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ in 15 ml of 1.2 *M* methanolic HCl.

By coordination of ethylene, **7** is converted to **4** (Scheme I) leading to another synthesis cycle. It will be noted that this reaction cycle does not invoke reversible oxidation of rhodium(I) by HCl (eq 11) which is considered an essential part of the mechanism of rhodium-catalyzed ethylene dimerization[3] and olefin isomerization.[13] In synthesis reactions with butadiene, the coordinated alkyl groups are either chelate or π-allyl structures, and these apparently stabilize rhodium(III).

$$\mathrm{rh^{I}} + \mathrm{HCl} \rightleftharpoons \mathrm{Hrh^{III}Cl} \qquad (11)$$

Although the proposed mechanism for 1,4-hexadiene *synthesis* does not involve exchange of solvent and olefin protons, exchange with reactant olefins proceeds concurrently. Thus, during conversion of 40% of an equimolar mixture of ethylene and butadiene to hexadienes in CH_3OD solution, 60% of the unreacted ethylene and 10% of the unreacted butadiene is partially deuterated. Presumably this occurs even though most of the rhodium is sequestered in hexadiene synthesis because exchange is much faster[13] than alkylation and requires very little catalyst. As a consequence of H–D exchange of the reactants, it is not possible to test the proposed synthesis mechanism by exchange studies.

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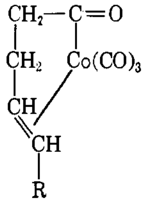
(12) Structurally related stabilized cobalt carbonyls



have been characterized by R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3116 (1963).

(13) R. Cramer, *ibid.*, **88**, 2272 (1966).

(14) It will be recalled that results in Figure 1 suggest that, in competitive coordination, ethylene would be favored over butadiene.

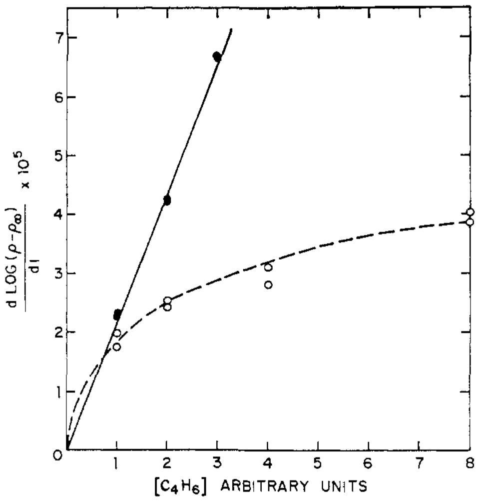


Figure 2. Effect of butadiene concentration on the rate of addition of ethylene to butadiene: solid line, 50°; dashed line, 30°.

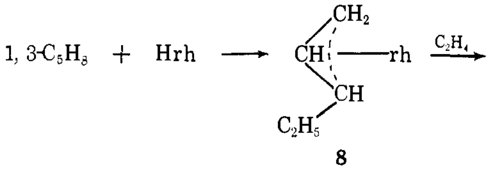
The nonintegral dependence of hexadiene synthesis on the concentration of butadiene at 30° indicates that at that temperature the rate of release of 1,4-hexadiene has increased relative to the rate of ethylene insertion. This is consistent with a greater concentration of **6** corresponding to the greater stability of olefin complexes of rhodium(III) at lower temperatures.[3]

Comparison of the Rates of Olefin Addition Reactions. Since the form of the rate expression changes with temperature, it is not possible to calculate an activation energy for inserting ethylene at a π-allyl ligand. It is, however, of some interest to compare the rates of olefin addition in several reaction systems.

In a reaction solution (methanol, 30°, [Rh] = 0.0167 *M*, [HCl] = 1.00 *M*) containing only ethylene, the pressure change corresponds to a first-order reaction for synthesis of 1-butene with the rate constant 1.24×10^{-4} sec^{-1}. In the presence of an eightfold excess of butadiene (so that the reaction is pseudo first order), but under otherwise identical conditions, the pseudo-first-order rate constant is 3.38×10^{-4} sec^{-1}, corresponding to synthesis of 1,4-hexadiene. This threefold difference in reaction rates cannot account for the preferential (about 50:1) formation of 1,4-hexadiene from equimolar mixtures of ethylene and butadiene and necessitates an alternative explanation such as the favored formation of **4**. If (as proposed) the rate of the insertion reaction (eq a, Scheme I) at 30° approximates the rate of release of 1,4-hexadiene (eq c, Scheme I), then the ratio of the rates of ethylene insertion in ethyl and π-crotyl complexes (eq 7) is about 1:3. This is not necessarily the ratio of the rate constants, however, since the rates depend upon the concentrations (which may be different) of the species $Rrh(C_2H_4)$ as well as the rate constants.

Dimerization of butadiene is much slower than either ethylene dimerization or hexadiene synthesis. In the catalyst solution described above, the rate of pressure change in the absence of ethylene (plotted as a first-order reaction) corresponds to a rate of 0.8×10^{-5} sec^{-1}.

Structure of Products of Addition of Ethylene to Conjugated Dienes. The structures of ethylene–diene addition products are consistent with the proposed mechanism. These correspond to 1,4 addition of hydrogen and a vinyl group to the diene system. In reactions of higher, 1,3-dienes the vinyl group is found on C_4, the more hindered position. It is suggested that this occurs because the structure of the product is determined during hydride addition, to give the π-allylic intermediate. For example, in the reaction of ethylene with 1,3-pentadiene, either of two π-allyl complexes, **8** or **9**, might be formed, leading to different products (eq 12 and 13). The actual product[1] corresponds to eq 13, thus indicating the π-allyl intermediate **9**. It has been shown[15] that this is the structure of the π-allyl group produced by addition of $HCo(CO)_4$ to 1,3-pentadiene. Similarly, the principal product from reaction of ethylene and isoprene corresponds to the π-complex with structure **10**. In view of the tendency of metal hydride addition to give minor amounts of *anti*-1-alkyl-π-allyl complexes,[15,16] formation of **10** rather than **11** might be anticipated.



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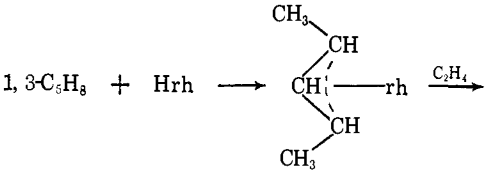
$$CH_2{=}CHCH_2CH{=}CHC_2H_5 \quad (12)$$



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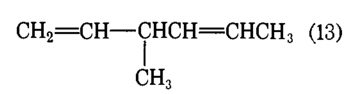
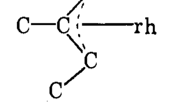


$$CH_2{=}CH{-}\underset{\substack{|\\ CH_3}}{C}HCH{=}CHCH_3 \quad (13)$$



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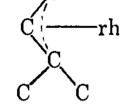

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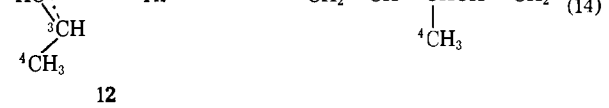
It might also be expected that some 3-methyl-1,4-pentadiene could be formed from ethylene and butadiene (eq 14) by ethylene insertion between ^3C and rhodium in **12**. A small amount (less than 1%) of this isomer appears in the C_6 diene product.[17]



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$$^{1}CH_2{=}^{2}CH{-}^{3}\underset{\substack{|\\ ^{4}CH_3}}{C}HCH{=}CH_2 \quad (14)$$

Charge on the Catalyst Molecule. It appears that the catalyst species involved in 1,4-hexadiene synthesis are

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(15) D. W. Moore, H. B. Jonassen, T. B. Joyner, and A. J. Bertrand *Chem. Ind.* (London), 1304 (1960).

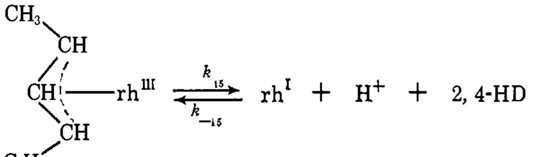
(16) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(17) Isolation and identification of this compound was accomplished by Dr. J. W. Collette of the Elastomer Chemicals Department of the Du Pont Co.

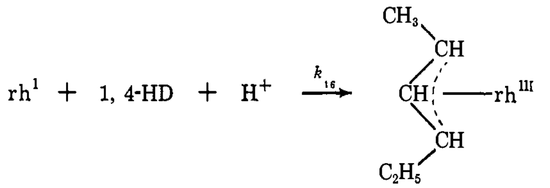
uncharged. This is inferred from the observation that rhodium is concentrated in the organic phase when ethylene and butadiene react in a medium consisting of 10% ethanol, 45% cyclohexane, and 45% water. Also a synthesis solution comprising 95% cyclohexane and 5% methanol remains homogeneous, whereas in the dimerization of ethylene, which is believed to involve ionic catalyst species, a second phase separates from mixtures containing less than 25% methanol.

Isomerization of 1,4-Hexadiene. 1,4-Hexadiene, the immediate product of addition of ethylene to butadiene, is isomerized to conjugated hexadienes (almost exclusively stereoisomers of 2,4-hexadiene) by rhodium catalyst solutions. When heated to 90° for 7 hr with a 0.01 M solution of $[(C_2H_4)_2RhCl]_2$ in 0.1 M methanolic HCl, 1,4-hexadiene yields 8% unreacted 1,4-hexadiene, 70% 2,4-hexadiene isomers, and 13% octadienes, plus small amounts of about 20 other species. A brief study of this reaction suggests it is consistent with rhodium-catalyzed monoolefin isomerization[13] modified by conjugated diene. Thus, 1-butene is rapidly isomerized at room temperature, and it is observed that, when 1,4-hexadiene is added to a solution of $[(C_2H_4)_2RhCl]_2$ in methanolic HCl, between 1 and 2 moles per mole of rhodium is isomerized within a few seconds at 25°; then reaction virtually stops. Further isomerization at a conveniently measurable rate requires temperatures of 70 to 90°. In a similar manner, 1,3-butadiene inhibits isomerization of 1-butene at 25°.[13]

Attempts to define the kinetics of hexadiene isomerization (assuming a clean reaction to 2,4-hexadiene) gave inconclusive results. A plot of $a \ln [1,4\text{-HD}]_i[1,4\text{-HD}]_t^{-1} - b([1,4\text{-HD}]_i - [1,4\text{-HD}]_t) = t$ is nearly linear during the first 50% of reaction. This is consistent with the scheme summarized by eq 15 and 16, assuming that equilibrium in (15) lies well to the left and $k_{-15} \approx k_{16}$.[18] However, a statistical analysis



(15)



(16)

shows that in these experiments the coefficients a and b are so covariant (the correlation matrix is generally larger than 0.9) that they cannot be used reliably to evaluate kinetic parameters or the reaction mechanism.[19] Empirically, the rate of isomerization at 70° of 0.5 M solutions of 1,4-hexadiene in 0.5 M methanolic HCl which is 0.001 to 0.01 M in Rh equals

$$0.4[\text{Rh}][1,4\text{-HD}]_{t=t}{}^{2}[1,4\text{-HD}]_{t=0}{}^{-1.2}$$

Isomerization of 1,4-hexadiene in CH_3OD at 90° leads to extensive exchange of solvent deuterium and olefin hydrogen.

Experimental Section

Induction Period in Hexadiene Synthesis with $RhCl_3$ Catalyst. A 400-ml bottle containing 0.15 g of "$RhCl_3 \cdot 3H_2O$" (0.6 mmole) in 0.6 ml of H_2O and 50 ml of CH_3OH was evacuated and an equimolar mixture of ethylene and butadiene was admitted at a pressure of 1350 mm. During 7 hr at 25° the average rate of pressure change was 4.4 mm hr^{-1}. After 18 hr the rate had increased to 20 mm hr^{-1}.

In a similar experiment in which a solution of 0.11 g of $[(C_2H_4)_2RhCl]_2$ (0.6 mg-atom of Rh) in 1.0 ml of concentrated aqueous HCl and 50 ml of CH_3OH was employed as catalyst, the initial rate of gas absorption was 35 mm hr^{-1}.

Synthesis and Chemistry of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$. a. Synthesis. $[(C_2H_4)_2RhCl]_2$ (14.6 g, 37 mmoles) was dissolved in 300 ml of 0.8 M methanolic HCl, and butadiene was bubbled through the stirred solution for 2 hr at 25°. The product, recovered by filtration and washed with methanol, weighed 13.3 g (27 mmoles, 73% yield) and could be recrystallized from chloroform. It decomposed without melting when heated above 100°.

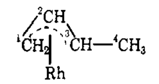
Anal. Calcd for $C_{12}H_{20}Rh_2Cl_4$: C, 28.16; H, 3.91; Cl, 27.71; mol wt, 511.8. Found: C, 28.41; H, 4.16; Cl, 27.90; mol wt (cryoscopic in benzene), 458, 472.

$(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ is sparingly soluble in $CHCl_3$ and CH_2Cl_2 and nearly insoluble in CH_3OH.

A KBr wafer absorbed at 2980 (w), 2920 (w), 1620 (m), 1538 (m), 1491 (w), 1450 (s), 1429 (s), 1373 (s), 1332 (w), 1311 (w), 1260 (w), 1197 (w), 1029 (s), 985 (br, s), 888 (m), 867 (br, m), 804 (br, w), 750 (br, m) cm^{-1}.

Nmr Spectrum. The solubility of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ in $CDCl_3$ is so low that a Varian C 1024 time-averaging computer was used in conjunction with the Varian A-60 spectrometer to record the nmr spectrum. The spectrum, which was poorly resolved, contained bands as shown in Table III. The chemical shifts correspond reasonably with assignments proposed for *syn*-π-crotylcobalt tricarbonyl;[15] however, the integrated areas at τ 3.6–4.0 and 5.5–6.2 were lower than the expected values (2 and 4, respectively).

Table III

τ value	Area	 Assignment
1.8–2.2	3	H on ^{4}C of π-crotyl group
3.6–4.0	1.1	H on ^{1}C of π-crotyl group
4.5–4.8	1.1	H on ^{3}C of π-crotyl group
5.5–6.2	3.4	H on ^{2}C of π-crotyl group and of coordinated butadiene

b. Chemistry. A 50-ml, round-bottomed flask containing 0.5 g (1.3 mmoles) of $[(C_2H_4)_2RhCl]_2$ and 15 ml of 1.2 M methanolic HCl was evacuated, and 150 ml (6 mmoles) of butadiene was admitted by gas buret to the stirred solution. Within 2 min a yellow solid separated, and at the end of 2 min 48 ml (2 mmoles) of gas was withdrawn. Mass spectral analysis showed it consisted of ethylene and butadiene in the mole ratio 7:5.

Hydrogenation. There was no reaction when a suspension of 0.25 g (0.49 mmole) of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$ in 20 ml of 0.15 M methanolic HCl was stirred with H_2 at 1 atm. Addition of 0.02 g of PtO_2 led to immediate absorption of 90.5 ml of H_2 (3.69 mmoles) during 40 min. Assuming 0.18 mmole was consumed in the reduction of PtO_2, 3.5 mmoles was required to reduce $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$. A mass spectrometric analysis showed the product was *n*-butane.

Attempts to isolate and characterize intermediate hydrogenation products were not successful. The complex dissolves after absorption of 2 moles of hydrogen with a small rate inflection when 4 moles of hydrogen has reacted, but solid products could not be isolated when the reaction was stopped at either stage.

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(18) *Cf.* L. P. Hammett, "Physical Organic Chemistry," 1st ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 107.

(19) The statistical analysis of these rate data was made by Mr. Richard Postles of the Engineering Dept. of the Du Pont Co.

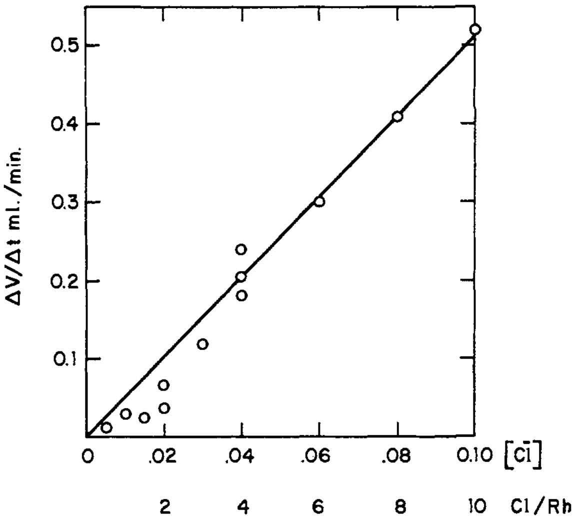

Figure 3. Effect of [Cl⁻] on the addition of ethylene to butadiene.

Butadiene Displacement. Reaction of 1 mmole of (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$ with 14 mmoles of $(C_6H_5)_3P$ in benzene or with 20 ml of aqueous ammonia (6 *M*) yielded 0.5 mmole of butadiene (identified by mass spectroscopy and infrared spectrum).

Cleavage with HCl. A mixture of 1 g of (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$ and 5 ml of concentrated, aqueous HCl was heated in a sealed tube at 100° for 0.75 hr. The gaseous product (25 ml) consisted of 68% 1-butene, 25% 2-butenes, and 10% butadiene (glpc analysis). The water-insoluble product consisted of 86% 2-chlorobutane and 14% 1-chloro-2-butene, identified by infrared and mass spectral analysis of samples separated by gas chromatography.

Reaction of Ethylene with (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$. A flask containing 0.35 g of (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$ (0.65 mmole) and 15 ml of 1.2 *M* methanolic HCl was evacuated and attached to a gas buret containing ethylene. The course of reaction is shown in Figure 1. About 2.5 mmoles of ethylene (after correction for the portion dissolved by methanolic HCl) reacted. The liquid hydrocarbon product was analyzed by glpc and contained 1,4-hexadiene, 2,4-hexadiene, and octadienes in the approximate ratio 1.1:0.7:1.

Cleavage with KOH. A mixture of 0.2 g of (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$ and 10 ml of 10% KOH in ethylene glycol gave a homogeneous solution but no gas was evolved (2 hr at 25°) until the solution was heated to 60°. This gas was identified as *trans*-2-butene by its infrared absorption.

Kinetic Studies of Olefin-Addition Reactions. The rate of olefin addition was measured through the pressure change accompanying reaction. The apparatus and procedure have been described in detail elsewhere.[3]

Experiments in Warburg Apparatus. The effect of [Rh], [Cl⁻], or [H⁺] was studied using a Warburg apparatus with $acacRh(C_2H_4)_2$ as the catalyst and a gas mixture consisting of 77 mole % butadiene and 23 mole % ethylene. The procedure for charging reactants was designed to avoid fractionation of the olefinic components. These were added at 30° to the reaction flask (with unmixed reaction solutions in flask side arms) while the manometers were temporarily immobilized by a plug of frozen mercury. Rhodium and hydrogen ion concentration had a similar effect upon the rate of addition of ethylene to butadiene to that which they had on ethylene dimerization.[3] However, the effect of chloride ion was different; reaction occurred at the lowest chloride concentration employed, and the plot (Figure 3) indicates that reaction occurs before the Cl⁻:Rh mole ratio becomes integral.

The Warburg apparatus was also used to study the effect of auxiliary ligands on addition of ethylene to butadiene. Separate compartments of Warburg flasks were charged with ethanol solutions of H_2SO_4, $acacRh(C_2H_4)_2$, and the ligand to be evaluated, and the procedure described earlier was employed. Each ligand was evaluated at five or more concentrations with ligand:Rh ratios from 1:1 to 20:1. Reaction occurred in systems containing NaCNO, urea, *n*-Bu_3P, and CN⁻ (the last two only at mole ratios of ligand:Rh of 1). Polybutadiene precipitated from all these reaction mixtures, its formation accounting for the observed pressure change. There was no reaction with dimethyl sulfoxide, *n*-Pr_2S, NaSCN, NaI, or $NaNO_2$. It is probable that hexadiene was produced in the presence of NaBr, but the rate was slower than with NaCl.

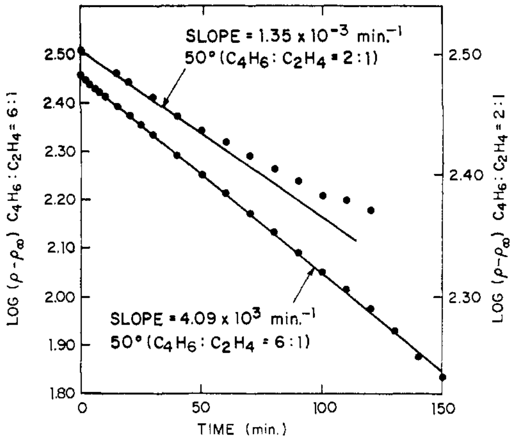

Figure 4. Rates of synthesis of 1,4-hexadiene.

Effects of temperature and olefin concentration were examined using apparatus described in connection with Figure 6 of ref 3. This was modified by connecting a 100-ml gas buret and a cylinder containing compressed butadiene between V_2 and J_1 of that figure. The method of introducing reactants was also modified slightly. The reaction flask, R, was charged with 30 ml of ethanolic HCl and chilled to −80°. Weighed, solid catalyst (sometimes $acacRh(C_2H_4)_2$ or $[(C_2H_4)_2RhCl]_2$ but usually (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$) was added. The chilled reaction flask, manometer, and connecting lines were evacuated. Ethylene and butadiene were metered into the cold reactor which was then positioned in a thermostated bath controlled to ±0.01°. Pressure over the stirred reactor was read periodically from M using a cathetometer.

Calculations were similar to those described in ref 3. Addition of ethylene to butadiene is essentially unidirectional.[20] Preliminary experiments showed that, although the data did not give persistent linear first-order plots, if the initial butadiene:ethylene ratio was greater than one, the first 10% of reaction approximated a first-order plot. Dependence on butadiene concentration was then calculated from the first-order rate constants obtained at various butadiene concentrations.

The pseudo-first-order constants were determined from plots of log $(P_t - P_\infty)$ against t (Figure 4). P_∞ was calculated on the assumption that, at $t = \infty$, ethylene would be converted to hexadienes and P_∞ would be the sum of the vapor pressure of ethanolic HCl and excess butadiene. The slopes of the plots divided by the fraction of ethylene in the liquid phase gave a set of first-order constants. A rate constant for an equation containing the concentration of butadiene as a parameter was calculated by dividing the pseudo-first-order constants by a power of the butadiene concentration which gave a fixed value for k over the range of butadiene concentration under consideration.

Table I summarizes a group of experiments at 50° with 1 mmole of rhodium (as (π-$C_4H_7)_2Rh_2Cl_4(C_4H_6)$), 30 ml of 1 *M* ethanolic

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(20) These calculations are based on data taken from F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Project 44, Carnegie Press, Pittsburgh, Pa., 1953, for reactions at 25°.

$$5C + 4H_2 \longrightarrow CH_2{=}CHCH_2CH{=}CH_2 \quad \Delta F = 40.69 \text{ kcal}$$

$$CH_2{=}CHCH_2CH_3 + C + H_2 \longrightarrow CH_2{=}CHCH_2CH_2CH_3 \quad \Delta F = 1.98$$

Therefore

$$6C + 5H_2 \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 \quad \Delta F \approx 42.67$$

since for 1-hexene → *trans*-2-hexene, $\Delta F = 2.31$. Therefore

$$6C + 5H_2 \longrightarrow CH_2{=}CHCH_2CH{=}CHCH_3 \quad \Delta F \approx 40.36$$

Since free energies of formation of ethylene and butadiene are 16.28 and 36.01

$$CH_2{=}CH_2 + CH_2{=}CHCH{=}CH_2 \longrightarrow trans\text{-}CH_2{=}CHCH_2CH{=}CHCH_3$$

$\Delta F \approx -11.93$ kcal, and $K = 8.6 \times 10^8$.

HCl, 100 ml of ethylene, and from 100 to 800 ml of butadiene. The listed butadiene concentration is 0.01 × ml of butadiene used. Experiments in Table II were run at 30° with 0.5 mmole of rhodium. The butadiene charge (in milliliters) was 200 × the listed arbitrary concentration. Other experiments, all run in 1 *M* ethanolic HCl, are summarized in Table IV.

Table IV. Rate of Addition of Ethylene to Butadiene

C_2H_4, ml	C_4H_6, ml	d ln $(P - P_\infty)$/d*t* × 10^5, sec^{-1}	Slope/$[C_4H_6]^{0.34}$ × 10^5 [a]
		(a) At 30°, 0.50 mg-atom of Rh	
50	600	8.4	5.0
100	600	8.8	5.2
175	600	8.8	5.2
		(b) At 50°, 0.50 mg-atom of Rh	
			Slope/$[C_4H_6]$ × 10^5 [b]
100	200	3.99, 4.07, 3.99	3.99, 4.07, 3.99
100	400	7.21, 7.82	3.61, 3.91
100	600	10.6, 12.3, 10.7, 11.5, 10.2, 11.6	3.53, 4.10, 3.57, 3.83, 3.40, 3.87
		(c) At 50°, 1.00 mg-atom of Rh	
100	400	11.5, 10.4, 9.96	5.75, 5.2, 4.98
150	400	10.4, 10.7	5.2, 5.35

[a] $[C_4H_6]$, in arbitrary units = 0.01 × ml of C_4H_6. [b] $[C_4H_6]$, in arbitrary units = 0.005 × ml of C_4H_6.

Reaction in CH_3OD. Using the apparatus employed to study the effect of temperature and olefin concentration on 1,4-hexadiene synthesis, a solution made from 0.13 g of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$, 25 ml of HCl gas, and 15 ml of CH_3OD was stirred with 300 ml of C_2H_4 and 300 ml of C_4H_6 (gas) at 50° until the pressure change indicated 40% conversion to hexadiene. Unreacted ethylene and butadiene were separated by distillation and analyzed by mass spectrometry. Ethylene consisted of 43% C_2H_4, 22% C_2H_3D, 17% $C_2H_2D_2$, 13% C_2HD_3, and 5% C_2D_4 (all ±2%). Butadiene was calculated to contain 91% C_4H_6, 8% C_4H_5D, and 1% $C_4H_4D_2$.

The rate of butadiene dimerization was measured using the apparatus employed for addition of ethylene to butadiene. The pressure change in systems containing 1 mg-atom of Rh in 1 *M* ethanolic HCl and 100 to 600 ml of butadiene does not correspond closely to either a first- or second-order reaction of butadiene at 30 or 50°. The change is so slow that it may be neglected in measuring the rate of addition of ethylene to butadiene. The value of *k* given in the discussion is based on a first-order rate plot.

The effect of 2,4-hexadiene on olefin additions was measured in the same apparatus. When 0.6 ml of 2,4-hexadiene was added to a reaction mixture containing 1 mg-atom of Rh and 30 ml of 1 *M* ethanolic HCl, the rate of ethylene absorption at 30° became 4% of the initial rate. At 50° the rate following addition of 0.6 ml (6 mmoles) of 2,4-hexadiene was 5% of the initial rate. Analysis by glpc of the reaction product after 75% reaction at 50° shows that about 50% of the ethylene combined with 2,4-hexadiene and 25% dimerized to butenes.

Although 2,4-hexadiene inhibits dimerization of ethylene it has little effect upon the reaction of ethylene with butadiene. Addition of 5 mmoles of 2,4-hexadiene to a solution of 0.5 mg-atom of Rh in 30 ml of 1 *M* ethanolic HCl and 100 ml each of butadiene and ethylene reduced the rate of reaction by about 15%.

The isomerization of 1,4-hexadiene was studied using the ultraviolet absorption of the conjugated diene in the product for analysis. A long-necked, 125-ml flask containing a magnetic stirrer was fitted with a capillary inlet which reached to the bottom of the flask and had an external stopcock. In a typical experiment, the flask was charged with 40 ml of 0.5 *M* HCl in ethanol and 2.00 ml of 1,4-hexadiene and chilled to −80°, and 0.039 g of $[(C_2H_4)_2RhCl]_2$ was added. The capillary inlet was sealed to the flask with polyphenylene oxide resin; the flask was tilted so that the bottom of the capillary was free of the solution, evacuated, and then pressured to 1 atm with nitrogen. Next, the flask was placed in a thermostated bath at 70° or 90 ± 0.05°. At intervals, 3-ml samples were withdrawn for analysis; the first 1 ml which had occupied the capillary inlet was discarded. Samples were diluted, and the transmittance at 226 mμ was measured in the range 0.35 to 0.75 using a Cary Model 10 spectrophotometer. Plots of various functions of the calculated concentration of 2,4-hexadienes against time indicate that the rate varies approximately with $[\text{1,4-hexadiene}]^2$, *i.e.*, plots of $[\text{1,4-hexadiene}]^{-1}$ *vs.* *t* are linear to 50% reaction. However, the slopes of these plots vary with the initial concentration of 1,4-hexadiene. As shown by the data in Table V, the rate of isomerization at 70° approximates $0.4[\text{Rh}][\text{1,4-hexadiene}]^2[\text{1,4-hexadiene}]_i^{-1.2}$ while the rate at 90° is given, less consistently, by $1.6[\text{Rh}][\text{1,4-hexadiene}]^2[\text{1,4-hexadiene}]_i^{-1.3}$ (subscript i designates initial concentration).

Table V. Rate of Isomerization of 1,4-Hexadiene

[Rh]	$[\text{1,4-HD}]_i$ [a]	d[1,4-HD]/d*t* × $[\text{1,4-HD}]_i^{1.2}$/[Rh]
	70°	
0.005	0.41	0.32, 0.48, 0.39
0.005	0.21	0.37
0.005	0.041	0.42, 0.37
0.0025	0.41	0.38
	90°	
0.005	0.41	1.31, 1.81, 1.51
0.005	0.21	1.14
0.005	0.041	1.64, 1.52
0.0025	0.41	2.12, 1.87

[a] $[\text{1,4-HD}]_i$ is the initial concentration of 1,4-hexadiene.

Hydrogen–Deuterium Exchange during Isomerization of 1,4-Hexadiene. A mixture of 1 ml of 1,4-hexadiene, 0.05 g of $(\pi\text{-}C_4H_7)_2Rh_2Cl_4(C_4H_6)$, 25 ml of HCl gas, and 10 ml of CH_3OD was stirred at 90° for 4 hr in a sealed, evacuated glass reactor. The hydrocarbon which separated when the mixture was diluted with 15 ml of water was dried over $CaCl_2$ and distilled *in vacuo* at 0°. According to glpc analysis it contained about 20% 1,4-hexadiene isomers, 50% 2,4-hexadiene isomers, and 20% octadienes in addition to 17 unidentified species in amounts up to 2%. Samples of 1,4-hexadienes and 2,4-hexadienes were collected by gas chromatography and analyzed for deuterium content by mass spectroscopy.

It is estimated that the 1,4-hexadiene contained 17% C_6H_{10}, 40% C_6H_9D, 30% $C_6H_8D_2$, 11% $C_6H_7D_3$, and less than 1% of several more highly deuterated isomers. The 2,4-hexadienes comprised 7% C_6H_{10}, 32% C_6H_9D, 34% $C_6H_8D_2$, 19% $C_6H_7D_3$, 6% $C_6H_6D_4$, and less than 1% each of several more highly deuterated hexadienes.