

Transition Metal Catalysis Exemplified by Some Rhodium-Promoted Reactions of Olefins

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A variety of organic reactions involving olefins, CO, and H₂ are catalyzed by solutions of transition metal compounds. Catalysis may be attributed to the ability of the metal ions to coordinate with reactant molecules, thereby both orienting them and reducing the energy barrier for bond making and breaking. Notably, the C-H bond of coordinated molecules when appropriately located with respect to the transition metal is unusually labile. Also, auxiliary ligands, although not ultimately incorporated in the product, may be critically important for catalysis. The rhodium-catalyzed syntheses discussed here (ethylene → butene, ethylene + butadiene → 1,4-hexadiene, and 1-butene → isomeric linear butenes) each comprise a characterizing sequence of reversible reaction steps. These steps, which are common to all three syntheses, are: (1) coordination of olefin with Rh(I) or Rh(III); (2) oxidative addition of HCl to Rh(I) to form a Rh(III) hydride; and (3) addition of coordinated hydride or alkyl to coordinated olefin to give, respectively, a coordinated alkyl or coordinated higher alkyl. In each synthesis system many combinations of these three steps are conceivable. The ability of the catalysts to produce clean products through thermodynamic or kinetic control is discussed for each synthesis.

The discoveries of ferrocene and Ziegler catalysts in 1951 awakened interest in the organic chemistry of transition metals. During the fifties most attention was given to the development of these two discoveries. But research of broader implications was also undertaken, including, notably, some very important work characterizing transition metal alkyls, olefin complexes, and related compounds by a group associated with Joseph Chatt. Around 1960 some of the newly organized chemistry was used to explain the cobalt carbonyl catalyzed synthesis of aldehydes from olefins, CO, and H₂. Since then, accelerated by information uncovered by such analytic techniques as infrared, nmr, chromatography, and mass spectroscopy, organo-transition metal chemistry has grown expansively. One reason for the interest which led to this growth is that a variety of syntheses, sometimes impressively selective, involving olefins, acetylenes, CO, and H₂ are catalyzed by transition metal compounds. These syntheses proceed through, and are understandable in terms of, the chemistry of organometallics, and it is expected (or, at least, hoped) that through increased understanding, catalysts may be designed whose specificity and efficiency will approach those of enzymes.

We will be concerned here almost exclusively with the mechanism of reactions of olefins that are catalyzed by compounds of Rh. Focusing on Rh catalysis is not as restrictive as it might appear, because if a compound of one transition metal is effective, generally compounds of other metals can be found which are also catalytically active. Catalysts based on four or more other metals have already been reported for each of the rhodium-promoted reactions described here.

Principles of Transition Metal Catalysis

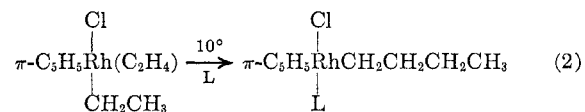
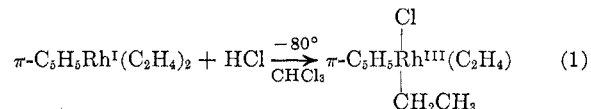
Since catalytic activity is shared only with compounds of transition metals, it is reasonable to seek for its explanation in properties peculiar to transition

Chart I
Indications of Ligand Activation

	Chemical evidence	Physical evidence
Activation of C=C	Easy addition to C=C	Infrared evidence for modified C=C
Activation of H	Displacement of H in M-QCH (Q = -CH ₂ -, -O-, -P-C=)	Unusual nmr chemical shift value for transition metal hydride

metals. Physical and chemical evidence indicates that catalytic effectiveness is a consequence of the ability of transition metals to: (1) coordinatively bond with and activate the carbon-carbon multiple bond, and (2) form metal-hydrogen bonds and activate carbon-hydrogen bonds of coordinated organic molecules. Examples of pertinent evidence are indicated in Chart I and discussed in the next few paragraphs.

Additions to C=C of coordinated olefins frequently occur with exceptional ease. For example, the formation of C-H and C-C bonds with ethylene coordinated to Rh, eq 1 and 2, occurs at -80 and 10°,¹ respectively.



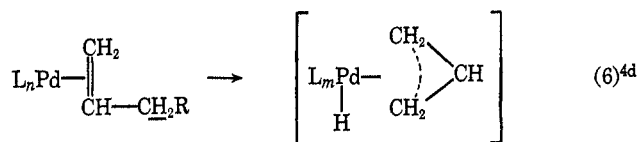
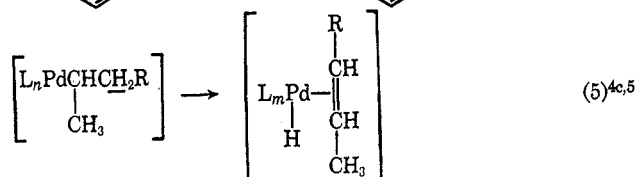
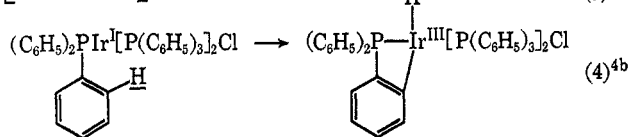
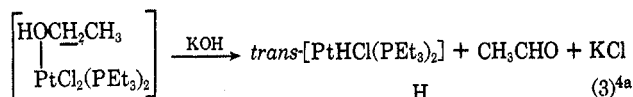
In contrast ethylene is relatively inert to HCl, CH₃I, CH₃Li, or, even, (C₂H₅)₃Al, which adds to ethylene only at temperatures above 70°.

Changes in the infrared absorption of olefins upon coordination indicate that reactivity of the olefin bond is enhanced. The C=C stretching frequency in olefin-

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

platinum complexes, for example, is lowered by about 140 wave numbers.² This may be attributed to an appreciable reduction of electron density which, like the electronegative group of α,β -unsaturated carbonyl compounds, renders the olefin susceptible to nucleophilic attack,³ an attack which can be further assisted by transfer of olefin electron density to the transition metal.

Hydrogen Activation. Hydrogen atoms at appropriate locations in organic ligands of transition metals are unusually labile yielding metal hydrides as products or product intermediates (eq 3-6). Since the carbon-



hydrogen bond is nearly ubiquitous in organic chemistry, the unusual ability of transition metal catalysts to assist in its breaking and making⁵ is particularly useful.

The metal hydrides have proton nmr absorptions in a higher range (+5 to +18 ppm, relative to tetramethylsilane) than any but a very few compounds. This suggests that hydrogen is highly shielded by the metal. Where measured, the metal-hydrogen bond is not abnormally short. However, calculations⁶

(2) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(3) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 2496, 3413 (1957); J. Tsuji and H. Takahashi, *J. Am. Chem. Soc.*, **87**, 3275 (1965); J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

(4) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962); L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 4989 (1962); (b) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967); (c) N. R. Davies, *Australian J. Chem.*, **17**, 212 (1964); M. Green, R. N. Hazeldine, and J. Lindley, *J. Organometal. Chem. (Amsterdam)*, **6**, 107 (1966); (d) R. Hüttel and H. Christ, *Chem. Ber.*, **96**, 310 (1963); **97**, 1439 (1964); W. R. Roth and W. Grimme, *Tetrahedron Letters*, 2347 (1966); M. Donati and F. Conti, *ibid.*, 4953 (1966).

(5) The hydrogen transfer reaction (eq 5) is, in principle, the reverse of eq 1 where catalytic activity is attributed to C=C activation. Equation 5 has been cited in support of hydrogen activation but C=C activation is equally applicable since a catalyst which lowers the energy barrier for addition of hydrogen to coordinated olefin (to give a metal alkyl) must also lower the barrier for the reverse reaction (conversion of a metal alkyl to the corresponding olefin complex). The combined effect may explain the extreme lability of β hydrogen in transition metal alkyls.

(6) R. M. Stevens, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962); see also A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 2747 (1964).

indicate that in $\text{HCo}(\text{CO})_4$ an appreciable amount of the electron density of 4s and 4p electrons extends outside a radius of 2.9 Å about cobalt. This accounts for the remarkable high-field chemical shifts in hydrides and could be responsible for activation of ligand hydrogen (eq 3-6).

Fundamentally, activation of hydrogen and multiple bonds is related to the ability, characteristic of transition metals, to supply or accept additional electrons, *i.e.*, to variable valence and coordination number. This property, illustrated in eq 1 and 4, has been discussed by various authors.⁷

Besides reducing the activation energy of organic reactions, transition metal ions assist syntheses by organizing the reactants⁸ through coordination bonds which are not strong enough to seriously bar their combination.

It is also relevant in a discussion of the principles of catalysis to point out that the auxiliary ligands in the catalyst species are critically important. For example, most of the Rh-catalyzed reactions which will be discussed here occur only in the presence of Cl^- , Br^- , or I^- . Auxiliary ligands may be involved in several ways. First, they may be electron conductors for the oxidation or reduction of the transition metal.⁹ This has been demonstrated in various organic reaction systems.¹⁰ Second, a coordinated ligand may assist in a displacement reaction at a C atom of a coordinated alkyl group.¹¹ Finally, ligands by induction and resonance help control the electron density of the transition metal at the level required for catalysis.¹²

Characteristic Reactions of Olefins Coordinated to Rhodium

Three Rh-catalyzed reactions of olefins will be described: (a) the dimerization of ethylene to 1-butene; (b) the addition of ethylene to 1,4-butadiene which yields 1,4-hexadiene; and (c) olefin isomerization involving double bond migration, for example, *cis*-2-butene to 1-butene and *trans*-2-butene. The same sorts of reaction steps are involved in all three reactions and a variety of products is conceivable; yet in each case the synthesis is well-controlled, kinetically and/or thermodynamically, to a clean product. Our strategy

(7) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 1679 (1962); R. F. Heck, *ibid.*, **86**, 2796 (1964); J. P. Collman and W. R. Roper, *ibid.*, **87**, 4008 (1965); P. B. Chock and J. Halpern, *ibid.*, **88**, 3511 (1966); C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

(8) G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963).

(9) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

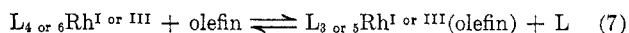
(10) E. Collinson, F. S. Dainton, B. Milne, S. Tazuke, and D. R. Smith, *Nature*, **198**, 26 (1963); J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, **87**, 522 (1965).

(11) R. E. Dessy and F. E. Paulik, *J. Chem. Educ.*, **40**, 185 (1963); J. K. Kochi and D. Buchanan, *J. Am. Chem. Soc.*, **87**, 853 (1965).

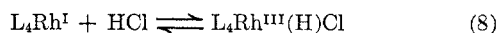
(12) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962); B. D. Babitzkii, B. A. Dolgoplosk, *et al.*, *Akad. Nauk SSR, Ser. Khim. Izv.*, 1507 (1965); P. Heimbach and W. Brenner, *Angew. Chem. Intern. Ed. Engl.*, **6**, 800 (1967); L. Porri, M. C. Gallazzi, and G. Vitulli, *Chem. Commun.*, 228 (1967).

will be first to consider the pertinent step-reactions of Rh-olefin complexes and then show how these fit together in each synthesis. The reaction steps are illustrated in eq 7-9. All are reversible. The equations are simplified since the formulas show specifically only the ligands which are transformed in the reaction. Other ligands are represented by L but generally are not all identical.

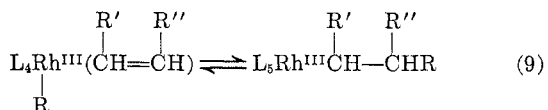
(a) Coordination of olefin to rhodium(I or III)



(b) Oxidative addition of HCl to rhodium(I)



(c) Addition of coordinated hydride or alkyl to coordinated olefin



(a) **Coordination of Olefin with Rhodium(I or III).**

This is an appropriate point to describe the generation of the catalyst.¹³ Usually rhodium is supplied as hydrated rhodium(III) chloride, which is activated through reduction to Rh(I) by substrate olefin or organic solvents, *e.g.*, ethanol. Reduction of Rh(III) is slower than the subsequent catalytic reactions and causes an induction period. As fast as Rh(I) is formed, it is converted to catalyst¹³ by reaction with olefin. With ethylene, for example, $L_2 \text{Rh}^{\text{I}}(\text{C}_2\text{H}_4)_2$ is produced. We will now consider some properties of olefin complexes, first of Rh(I), then of Rh(III).

The ethylene-Rh(I) bond is strong (thermodynamic) but usually very labile (kinetic). For example, $\text{acac-Rh}^{\text{I}}(\text{C}_2\text{H}_4)_2$ does not dissociate appreciably in glycol solution at 80°, but it exchanges ethylene faster than 10^4 sec^{-1} at 25°.¹⁴ Ethylene may also be displaced rapidly by other olefins or by ligands of the same type,¹⁵ *e.g.*, CO, CN⁻, pyridine, phosphines. Among hydrocarbon monoolefins, ethylene coordinates most strongly (ethylene:butene $\approx 1000:1$),¹⁶ but it is completely displaced by CO, CN⁻, pyridine, phosphines, and chelating dienes such as 1,5-cyclooctadiene. *Selective olefin coordination by Rh(I) in an exchange far faster than the overall synthesis is one means by which the catalyst controls the course of reaction.*

Olefin complexes of Rh(III) are less stable than those of Rh(I). In 1 M ethanolic HCl under 1 atm of ethylene, $\text{C}_2\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_4$ is 80% dissociated (to $\text{C}_2\text{H}_5\text{RhL}_5$ and ethylene).¹ Exchange of ethylene on Rh(III) is fast compared with any of the syntheses discussed here, but it is slower than ethylene exchange of Rh(I) compounds.

(b) **Oxidative addition of HCl to a Rh(I) compound**

(13) Catalyst is defined here as any of the Rh-containing species in the synthesis cycle. Thus in a four-step reaction any of four rhodium-containing intermediates might be termed "catalyst."

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

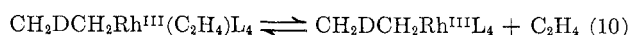
(15) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

(16) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).

is believed to generate a rhodium(III) hydride although in these synthesis systems hydride formation can only be inferred from other evidence. The hydride ligand cannot be detected, apparently because the Rh(I) compound which is attacked by HCl has an olefin ligand and hydride adds to coordinated olefin instantaneously according to eq 9. However, a hydride may be isolated when Rh^I does not have an olefin ligand, *e.g.*, when $L_4 \text{Rh}^{\text{I}}$ is $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}$.¹⁷ When $L_4 \text{Rh}^{\text{I}}$ is $\pi\text{-C}_5\text{H}_5\text{Rh}^{\text{I}}(\text{C}_2\text{H}_4)_2$, addition of HCl is too fast in CH_3Cl solution to measure by conventional means at -80°. (Even at -80°, hydride adds to coordinated ethylene so fast that hydride is not detected; the observed reaction is that shown by eq 1.)

(c) **Addition of coordinated hydride or alkyl to coordinated olefin** is frequently termed olefin "insertion."¹⁸ If R is H and $\text{R}'\text{CH}=\text{CHR}''$ is C_2H_4 , equilibrium in eq 9 lies so far to the right that metal hydride cannot be detected by nmr. Further, there is no evidence of C_2H_4 over a solution of $[\text{C}_2\text{H}_5\text{Rh}^{\text{III}}\text{L}_5]$ (where $L \neq \text{C}_2\text{H}_4$), which by reversal of eq 9 could yield an unstable ethylene complex of Rh(III). Nevertheless, the system indicated by eq 9 is very labile, as is shown by the dissolution of $[\text{Cl}_2\text{Rh}^{\text{I}}(\text{C}_2\text{H}_4)_2]^-$ in $\text{CH}_3\text{OD}-\text{DCl}$.

When $[\text{Cl}_2\text{Rh}^{\text{I}}(\text{C}_2\text{H}_4)_2]^-$ is dissolved in $\text{CH}_3\text{OD}-\text{DCl}$, ethylene is evolved immediately and rapidly. This is a consequence of oxidative addition of DCl (eq 8) followed in succession by addition of D to coordinated ethylene (eq 9) and loss of ethylene from the resulting unstable ethylene compound of Rh(III) (eq 10).



But the evolved ethylene is highly deuterated containing, typically, about 20% C_2D_4 . Monodeuterioethylene could be formed (through the reverse of eq 9 with H migrating rather than D) and released from its relatively unstable complex with Rh(III) (analog of eq 10). But the synthesis of polydeuterated ethylene implies further exchange of H and D through coordination of $\text{CH}_2=\text{CHD}$ to Rh(I) (eq 7) followed by oxidative addition of DCl to that Rh(I) complex (eq 8), then the addition of coordinated D to coordinated $\text{CH}_2=\text{CHD}$ (eq 9), and finally formation of a complex of $\text{C}_2\text{D}_2\text{H}_2$ through a reversal of eq 9. The appearance of C_2D_4 in the evolved gas (within seconds) requires that reactions 7, 8, and 9 be very fast.

If hydride adds to a higher, terminal olefin (eq 9) it generally attacks the β -carbon atom and Rh is bonded to the terminal carbon. Specifically, with 1-butene the ratio $L_5\text{RhCH}_2\text{CH}_2\text{C}_2\text{H}_5:L_6\text{RhCH}(\text{CH}_3)\text{C}_2\text{H}_5$ is >15 .¹⁹

(17) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(18) The term "olefin insertion" implies olefin mobility and is misleading since with respect to other ligands attached to the metal, olefin probably does not move and the newly formed alkyl group is attached at the position formerly occupied by olefin. It is R of eq 9 (either H or alkyl) which moves to the new position [cf. K. Noak and F. Calderazzo, *J. Organometal. Chem. (Amsterdam)*, **10**, 101 (1967)].

(19) R. Cramer, *J. Am. Chem. Soc.*, **88**, 2272 (1966).

The relative amounts of linear and branched alkyl formed when coordinated hydride adds to coordinated olefin is a second way by which the catalyst directs the synthesis.

While it is clear that the Rh(I) complexes of higher olefins are less stable than that of ethylene, the effect of olefin branching on the equilibria described by eq 8 and 9 is uncertain. A consistent interpretation of experiments follows if it is assumed that alkyl substituents on either α or β carbon destabilize $L_3Rh^{III}-CH_2CH_3$ and the effect is cumulative.²⁰

When R is an alkyl group rather than H (eq 9), addition to coordinated olefin is much slower. Specifically, the addition of coordinated C_2H_5 to coordinated ethylene is observable but slow at 10° (compared with very fast addition of hydride at -80°). No evidence has been seen for C-C cleavage in a rhodium alkyl (reverse of eq 9) but such cleavage has been proposed²¹ in a related nickel-catalyzed reaction.

This completes the description of the intermediates and their step-reactions, and we proceed to a discussion of how the pieces fit together in three rhodium-catalyzed syntheses.

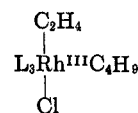
Rhodium-Catalyzed Syntheses

Dimerization of ethylene in the presence of a Rh catalyst occurs at 25° (1 atm) and, on a preparative scale, is conveniently run at 50° (100 atm). The immediate product is 1-butene, but under usual synthesis conditions 70% or more of this is isomerized to 2-butenes during synthesis. Conversion to hexenes and higher olefins can be kept below 1%.²² A cyclic synthesis scheme, shown in Scheme I, is made up of the reaction steps described earlier (eq 7-9).

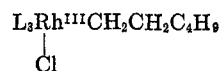
The rate-determining step is addition of coordinated ethyl to coordinated ethylene (eq b, Scheme I). This

conclusion was reached through isolation and comparison of the rates of the individual steps and is consistent with the kinetics of the overall reaction.¹ Synthesis of 1-butene will not be discussed further since it is believed that Scheme I is self-explanatory when studied in conjunction with the section "Characteristic Reactions of Olefins Coordinated to Rhodium." But consideration of two points may be useful: (1) Why are butenes formed to the virtual exclusion of higher olefins? (2) What controls the extent to which 1-butene is isomerized during synthesis?

The answers are to be found in the rates and equilibria of the pertinent characteristic reactions. Considering first the possible formation of higher olefins, it is plausible that **4** (Scheme I) might coordinate with ethylene giving



and this by rearrangement to

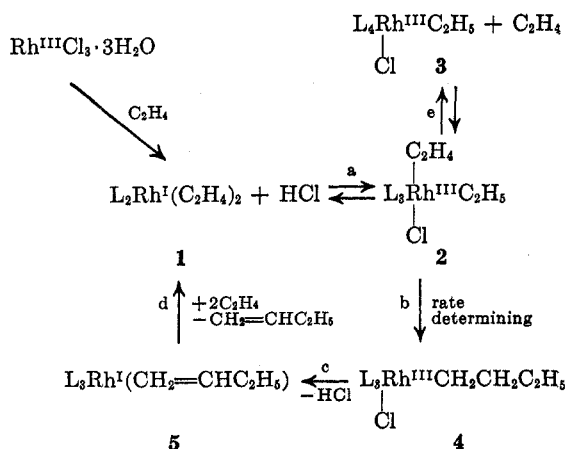


(eq 9) could yield hexene. However, in the Rh system addition of coordinated alkyl to coordinated olefin is a slow reaction; before it has time to occur, **4** is converted to **5** (eq c, Scheme I) and then (favored by a large equilibrium constant) 1-butene is immediately displaced by ethylene.

Ethylene has been dimerized using compounds of Ti,^{23a} Pd,^{23b} Co,^{23c} Ni,^{23d} or "other metals of groups IV to VIII" (as π -allyl complexes)^{23e} for the transition element catalyst component. It is not surprising that among these, the element which yields a practical ethylene polymerization catalyst, Ti, has the greatest tendency to induce multiple ethylene additions giving higher oligomers.

Incomplete isomerization of 1-butene during its synthesis is a consequence of a competition between kinetic and thermodynamic control. Isomerization is much faster than dimerization, so 1-butene might be expected to isomerize as it is formed. However, coordination of the substrate for dimerization (ethylene) is favored by a factor of about 1000 over the isomerization substrate (1-butene), so thermodynamics favors dimerization. By stopping the synthesis when 50% of the ethylene has reacted, a product containing 40% 1-butene is obtained compared with about 4% 1-butene in equilibrated linear butenes.

Scheme I
Scheme for Dimerization of Ethylene



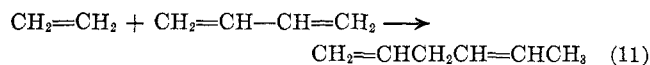
(20) It has been reported that attempts to prepare $\eta\text{-C}_7\text{H}_{13}\text{Pt}[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{Cl}$ yielded $\text{HPt}[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{Cl}$ [J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc., A*, 190 (1968)]. The corresponding $\eta\text{-C}_7\text{H}_{13}\text{Pt}[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{Cl}$ is accessible.

(21) R. G. Miller, *J. Am. Chem. Soc.*, **89**, 2785 (1967).

(22) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *ibid.*, **87**, 5638 (1965); T. Alderson, U. S. Patent 3,013,066 (1961).

(23) (a) H. Bestian and K. Clauss, *Angew. Chem. Intern. Ed. Engl.*, **2**, 704 (1963); K. Shikata, *et al.*, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **68**, 2266 (1965); (b) J. T. Van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964); J. Smidt, W. Hafner, and J. Sedlmeier, German Patent 1,193,934 (1965); Y. Kusunoki, R. Katsuno, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **39**, 2021 (1966); A. D. Ketley, *et al.*, *Inorg. Chem.*, **6**, 657 (1967); (c) G. Hata, *Chem. Ind. (London)*, 223 (1965); (d) Shell International Research, French Patent 1,385,503 (1964); M. Tsutsumi and T. Kozano, *J. Polymer Sci., A-1*, **5**, 681 (1967); (e) G. Wilke, French Patent 1,410,430 (1965).

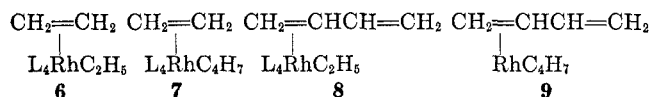
Addition of Ethylene to Butadiene. Reaction of a mixture of ethylene and butadiene in the presence of a Rh catalyst yields 1,4-hexadiene²² (eq 11). This can



be pictured as 1,4-addition of ethylene as $\text{CH}_2=\text{CH}-$ and H to the conjugated double bonds of butadiene. The synthesis is of considerable technical interest because the product can be copolymerized with ethylene and propylene to an elastomer which is vulcanizable by conventional sulfur cures.

Although ethylene is not consumed faster in this reaction with butadiene than it is by dimerization, practically no butene is formed in the presence of butadiene. In this case it appears that the synthesis is unidirectional as a consequence of thermodynamic control. Considering eq 9, substrate olefin may appear in two roles in the catalyst molecule which is about to rearrange—as the alkyl group, R, and as olefin ligand, $\text{R}'\text{CH}=\text{CHR}''$. When a mixture of two olefins is employed, four situations are conceivable as indicated in Chart II. There is evidence to show

Chart II
Possible Structures for Chain Growth
in Ethylene-Butadiene Mixtures



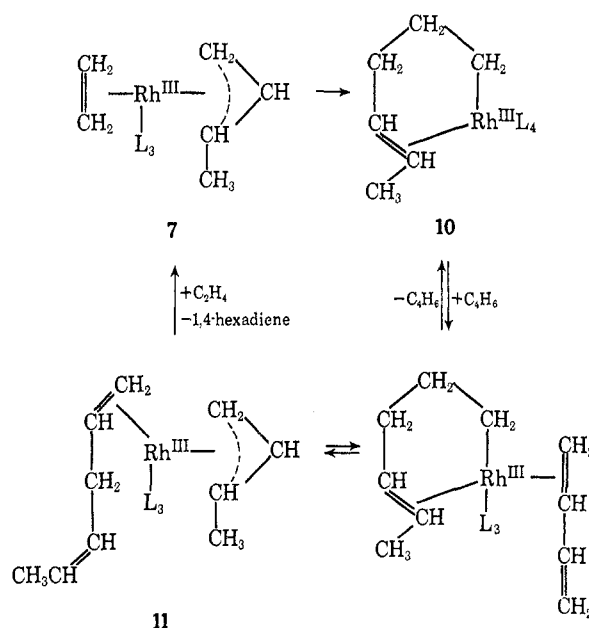
that species **7** is the most stable.²⁴ Since the reactions which lead to formation of the species of Chart II are much faster than their rearrangement by eq 9, the high concentration of species **7** leads to exclusive formation of 1,4-hexadiene even though insertion reactions of **6** and **7** appear equally fast.

An interesting difference in the mechanisms of ethylene dimerization and ethylene addition to butadiene appears when the kinetics of the latter reaction is scrutinized.²⁴ It was stated earlier that in ethylene dimerization the insertion reaction (eq b, Scheme I) is rate determining. In the addition of ethylene to butadiene, although the rate of insertion is nearly as slow as the rate-determining step, insertion ceases to be rate determining as the synthesis temperature increases from 30 to 50°. It appears that the chelated compound **10** (Scheme II) formed by addition of a butenyl group to coordinated ethylene is so stable that its release (through transfer of hydrogen to butadiene and formation of the approximately equally stable π -crotyl complex, **11**) becomes rate determining at the higher temperature. Consequently, although initial reduction of Rh(III) is required for activation, the reaction scheme (Scheme II) does not involve a cyclic valence change for Rh as was invoked for butene synthesis (and will be proposed later for olefin isomerization).

Hexadiene synthesis from ethylene and butadiene is

(24) R. Cramer, *J. Am. Chem. Soc.*, **89**, 1633 (1967).

Scheme II
Scheme for Addition of Ethylene to Butadiene



also catalyzed by systems containing compounds of Co,^{25a} Fe,^{25b} Ni,^{25c} or Pd.^{25d}

When butadiene alone is treated with the Rh catalysts used to dimerize ethylene or to add ethylene to butadiene, butadiene dimers are formed. In addition, Rh compounds have been used to polymerize butadiene. Although precisely comparable data are not available, the rate of polymerization of butadiene in dimethylformamide²⁶ is the same order of magnitude as the rate of its dimerization in methanol. So it is permissible to speculate that the mechanisms of chain growth are the same in dimerization and polymerization and ask what distinguishes dimerization catalyst from polymerization catalyst. A possible explanation is the presence of coordinated Cl^- in the dimerization catalyst. Chloride-free Rh salts are preferred as catalysts for polymerization, and if rhodium(III) chloride is used, the only reported effective systems are aqueous media which are so dilute that aquation of Rh can reasonably be assumed complete. In alcohol, where solvolysis is expected to be less extensive, rhodium(III) chloride does not catalyze polymerization.²⁷ A reasonable conclusion is that coordinated Cl^- stops polymer chain growth, possibly by assisting hydrogen transfer (reverse of eq 9).

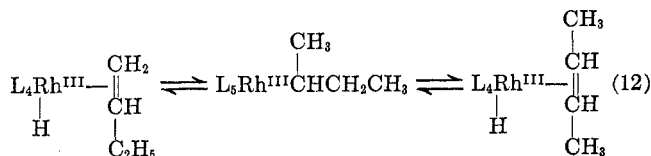
Isomerization of olefins (double bond migration or *cis-trans* isomerization) is catalyzed by compounds of all the first row transition metals, of all the group VIII

(25) (a) D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); Toyo Rayon, French Patent 1,462,308 (1966); (b) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964); M. Iwamoto and S. Yaguchi, *J. Org. Chem.*, **31**, 4290 (1966); A. Carbonaro, A. Greco, and G. Dall'asta, *Tetrahedron Letters*, 2037 (1967); (c) T. J. Kealy, French Patent 1,388,305 (1964); (d) B. F. Goodrich, Netherlands Patent 66,09107 (1966).

(26) C. E. H. Bawn, D. G. T. Cooper, and A. M. North, *Polymer*, **7**, 113 (1966).

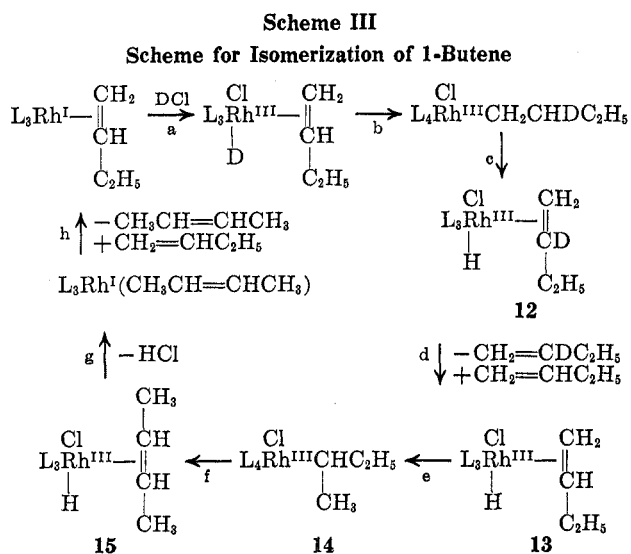
(27) R. E. Rinehart, H. P. Smith, H. S. Witt, and H. Romeyn, *Jr.*, *J. Am. Chem. Soc.*, **84**, 4145 (1962).

metals, and of many other transition metals. Rhodium-catalyzed isomerization is faster than ethylene dimerization or addition to butadiene and is observable at -25° . This is consistent with a reaction scheme involving hydride addition to coordinated olefin (eq 12) which is expected to be faster than alkyl addition (eq 9).

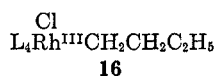


While eq 12 describes the mechanism of rhodium-catalyzed olefin isomerization superficially, it ignores important details. Thus, studies of the isomerization of 1-butene in CH_3OD revealed¹⁹ two mechanistically important facts: (1) approximately one deuterium atom is exchanged for each molecule of butene that is isomerized; (2) most of the deuterium is found in $\text{CH}_2=\text{CDC}_2\text{H}_5$, although some $\text{CH}_3\text{CH}=\text{CDCH}_3$ and $\text{CH}_2\text{DCH}=\text{CHCH}_3$ are also formed.

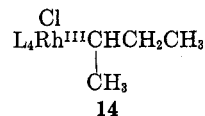
These results are consistent with Scheme III.



Steps a, b, and c are relatively straightforward examples of eq 8 and 9. Step d, by which $\text{CH}_2=\text{CDC}_2\text{H}_5$ is liberated from Rh, conforms with the ability of Rh(III) olefin complexes to undergo reversible olefin dissociation.¹ The high concentration of $\text{CH}_2=\text{CH}-\text{C}_2\text{H}_5$ relative to $\text{CH}_2=\text{CDC}_2\text{H}_5$ favors the exchange. Steps e and g of Scheme III require some comment. First, step e. Generally (about 15 times in 16) the addition of hydride to coordinated 1-butene gives

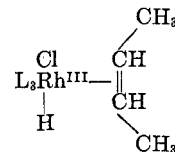


instead of

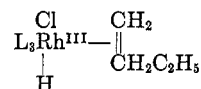


But the reverse reaction of **16** can only lead back to the initial 1-butene complex, **13**. The only forward-going reaction is e. In effect (and on the average) about 15 steps leading to **16** and their reversal (which occur before e does) have been omitted from Scheme III.

Next, step g. Scheme III fits experimental data if **15** loses HCl (reverting to a compound of Rh(I)) instead of exchanging coordinated 2-butene for substrate 1-butene (by a reaction analogous with d). No independent evidence is available to support this proposal. It could result if



either lost HCl more readily or exchanged butene more slowly than



Both explanations can be rationalized but not compellingly.

The final step of the isomerization in Scheme III, displacement of 2-butene from rhodium(I) by 1-butene (eq h), is expected from data on the relative stabilities of complexes of these olefins with Rh(I).¹⁶ Isomerizations of *cis*-2-butene and *trans*-2-butene give results which are consistent with Scheme III and implement evaluation of the relative rates of some of the steps.

Insertions (eq b and e, Scheme III) are certainly not rate determining in isomerization as they are for ethylene dimerization. In methanol, which competes for proton, the probable rate-determining reaction of isomerization is addition of HCl to Rh^I (eq a).

Isomerization studies using compounds of other transition metals as catalysts indicate that exchange of olefin hydrogen with D⁺ is a general reaction and may be either more or less extensive than isomerization.²⁸ The ratio H-D exchange:isomerization (approximately 1:1 in rhodium-catalyzed isomerization) is about 1:100 for some Ni and Pd catalysts and 1.5:1 for a Pt catalyst. The results may be interpreted in terms of Scheme III if it is assumed that the Ni or Pd intermediate corresponding to **15** exchanges its 2-butene (for 1-butene) faster than it loses HCl (eq g) while the Pt intermediate corresponding to **12** or **13** loses HCl faster than it is converted to **14**.

(28) R. Cramer and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **88**, 3534 (1966).