The Dimerization of Alkenes by Palladium and Rhodium Chlorides

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Ethylene and propylene are dimerized by palladium chloride under mild conditions in a number of solvents. These solvents are shown to catalyze both the formation and isomerization of π complexes of the olefins with the salt. The π complex which is the active species in the dimerization is converted, as the reaction proceeds, into an inactive π-allyl complex. Rhodium chloride is effective in the same solvents. However, the mechanism of dimerization by this compound appears to be different from that using palladium chloride.

Introduction

Recently, a number of systems have been described in which transition metal salts and complexes are active catalysts for the dimerization and oligomerization of olefins. Cramer has studied the dimerization of ethylene by rhodium chloride in ethanol in considerable detail and has shown that this reaction, which is acid catalyzed, proceeds by insertion into a rhodium alkyl σ bond.[1] Alderson and co-workers have extended this reaction to the addition of ethylene and propylene to various dienes.[2] Very active catalysts for both ethylene and propylene dimerization obtained by allowing π-allylnickel halides to react with aluminum chloride have been described by Wilke.[3] The dimerization of ethylene by di-μ-chloro-dichlorobis(ethylene)dipalladium in benzene and dioxane has been observed by van Gemert and Wilkinson.[4]

The dimerization of ethylene by palladium chloride, which proceeds by the intermediate formation of di-μ-chloro-dichlorobis(ethylene)dipalladium, was found independently by us using as reaction media certain chloro and nitro compounds which exert a marked catalytic effect. The mechanism of this dimerization and also that of propylene is discussed below. Some comparison is made with the results of dimerizations carried out under similar conditions with rhodium chloride.

Results and Discussion

Dimerization of Ethylene by PdCl₂.—When dimerizations were carried out using 1.5 g of $PdCl_2$ slurried in $CHCl_3$ as a reaction medium, under 10 atm of ethylene pressure at 50°, the $PdCl_2$ was completely converted to a yellow complex in 30 min. This was identical with di-μ-chloro-dichlorobis(ethylene)dipalladium (I) prepared by the method of Kharasch.[5] In the only reported direct preparation of I, $PdCl_2$ was suspended in benzene and treated with 60 atm of ethylene for 8 hr.[6] Only partial conversions were obtained. Compound I is formed at about the same

rate in carbon tetrachloride, methylene chloride, nitrobenzene, and nitroalkanes. All of these materials, therefore, exert a catalytic effect. However, the most striking effect is obtained in ethyl and *t*-butyl chlorides. When $PdCl_2$ is suspended in either of these media, conversion to I under 10 atm of ethylene pressure is complete in <1 min at room temperature.

If $CHCl_3$ containing trace (0.03 M) ethanol as stabilizer is used as the reaction medium, the initially formed yellow complex goes into solution ($\sim$24 hr). The clear, homogeneous, red solution thus formed yields, under the above conditions, approximately 0.1 mole/hr of a mixture consisting of 52% *trans*-2-butene, 47% *cis*-2-butene, and 1% 1-butene. In the absence of ethanol, only compound I is formed. Methanol, isopropyl alcohol, *t*-butyl alcohol, and water (0.02–0.1 M) all catalyze the dimerization in chloroform, the rate being essentially independent of the compound used. Within the range cited, the rate is also independent of concentration. However, concentrations in excess of 0.1 M (that is >1:1 ratio of $ROH:PdCl_2$) deactivate the catalyst with the formation of palladium metal. In all of these $CHCl_3$–ROH systems the reaction of $PdCl_2$ with ethylene to give I requires $\sim$30 min at 50° or 2 hr at 30°. However, when 0.05 M ethylene glycol in chloroform is used, I forms in <15 min at 30°.

In a number of other media, notably methylene chloride, nitrobenzene, and nitroethane, formation of I followed by conversion to the red solution and formation of dimer occurs in the complete absence of any hydroxylic additive. In other media, for example, carbon tetrachloride, alkyl halides, and saturated hydrocarbons, compound I remains unaffected by ethylene and can be recovered unchanged after several days. Only small amounts of dimer are formed in these latter systems. Addition of alcohols or water to the inactive media (with the exception of chloroform) does not catalyze dimer formation.

When ethylene is removed from the system ($CHCl_3$–ROH, CH_2Cl_2, RNO_2) after the initial formation of I, the palladium chloride–ethylene complex can be isolated by filtration in >95% yield. We found, however, that when ethylene was removed from the system at 20 hr, the yellow precipitate, which we had assumed

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

(2) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *ibid.*, **87**, 5638 (1965).

(3) G. Wilke, B. Bogdanovic, P. Hardt, P. Heinbach, W. Keim, M. Kroner, W. Oberkerch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

(4) J. T. van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

(5) M. S. Kharasch, R. C. Seyler, and F. R Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

(6) W. M. MacNevin and S. A. Giddings, *Chem. Ind.* (London), 1191 (1960).

to be unchanged I, dissolved rapidly. (All information relates to runs carried out at 50°. Similar results were obtained at 30°, but reaction times were ~3.5 times greater than these given in this paper.) The precipitate re-formed on repressuring the system with ethylene. The solution obtained on removing ethylene appeared to be stable since after 3 days precipitate again formed on adding ethylene. Since I is insoluble in the reaction media, the yellow solid present at 20 hr was obviously a different compound.

An attempt was made to isolate the new compound (II) by cooling the reaction vessel to −40° before removing ethylene. Under these conditions, II did not dissolve and could be collected by filtration. However, when the material collected in this way was analyzed by X-ray crystallography, infrared, and elemental analysis, it proved to be compound I. The cooled mixture was then filtered in the apparatus shown in Figure 1 which enabled II to be kept at −40° on the filter. The precipitate was dried under these conditions in a stream of cooled argon and then the apparatus was connected to a gas collection system. When II was allowed to come to room temperature, it evolved ~2 moles of ethylene (analyzed by mass spectroscopy) for every mole of I collected.
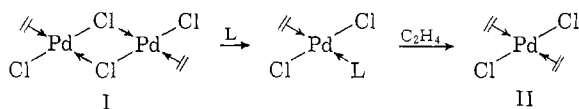
The rate of formation of II was followed by removing ethylene at room temperature and filtering off excess I. The solution was then repressured with ethylene to precipitate II and cooled to −40°. Compound II was filtered at −40° and dried; then the volume of ethylene evolved when II was brought to room temperature was measured. Some results of these experiments are shown in Table I.

Figure 1.—Apparatus for isolating $(C_2H_4)_2PdCl_2$.

TABLE I

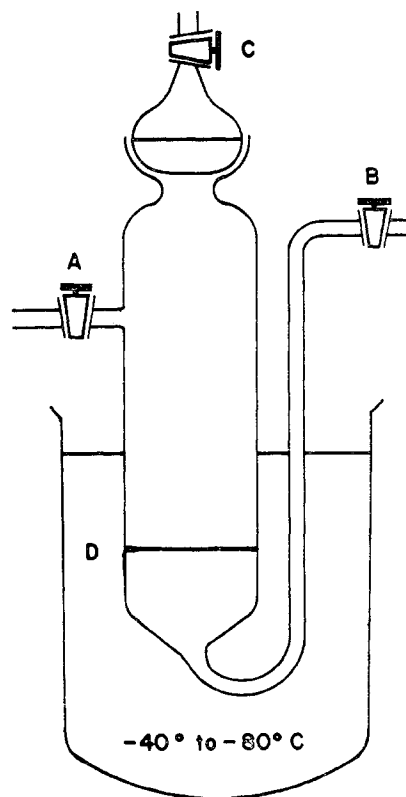|	Reaction time, hr			
	4	6	12	22
C_2H_4 evolved by II,[a] ml	74	88	120	192
$(C_2H_4)_2Pd_2Cl_4$, g	0.6	0.8	1.2	1.6
Mole ratio, (C_2H_4) (evolved)/ $(C_2H_4)_2Pd_2Cl_4$	2.2	2.0	1.9	2.2

[a] Corrected for thermal expansion of argon in system by carrying out blank runs.

Compound II is too unstable to analyze by spectroscopic means. It seems reasonable to assume, however, on the basis of Chatt's results for the reaction of ethylene with di-μ-chloro-dichlorobis(ethylene)diplatinum, that II has the structure shown in the reaction sequence[7]


Breaking of the chlorine bridges is presumably facilitated by solvents which can act as weak ligands or by additives such as ethanol. It is not clear why ethanol is not effective in the case of carbon tetrachloride or alkyl halides.

Compound II dissolves rapidly upon removal of ethylene as described above. The solution from a re-

action in methylene chloride was concentrated under vacuum until solid began to separate. On standing, red crystals were obtained which readily redissolved in methylene chloride to give a clear solution which precipitated II under pressure. Figure 2 shows the pmr spectrum of this compound (III) compared with that of a complex prepared by adding butene-2 to I (compound IV). Compound IV (*Anal.* Calcd for $C_8H_{16}Pd_2Cl_4$: C, 20.57; H, 3.43; Cl, 30.53; Pd, 45.47. Found: C, 20.38; H, 3.41; Cl, 30.40; Pd, 45.2) almost certainly has the structure[8]

IV
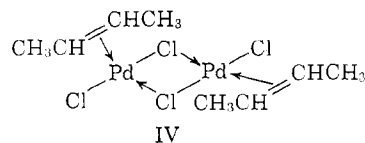
Both the pmr and infrared spectra (strong band at 1520 cm^{-1}) of this compound support this view.[9] Compound III (*Anal.* Calcd for $C_8H_{16}Pd_2Cl_4$: C, 20.57; H, 3.43; Cl, 30.53; Pd, 45.47. (Found: C, 20.04; H, 3.18; Cl, 30.18; Pd, 45.78) has the same empirical formula, pmr, and infrared spectra. However, it is approximately 20 times as soluble in CH_2Cl_2 as IV and is converted rapidly (~1 min) to compound II by ethylene pressure while IV is not. Furthermore, compounds III and IV give different X-ray powder diagrams. We believe that compound III has the structure shown and is formed by reaction of II with

(7) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

(8) J. N. Dempsey and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4984 (1955).

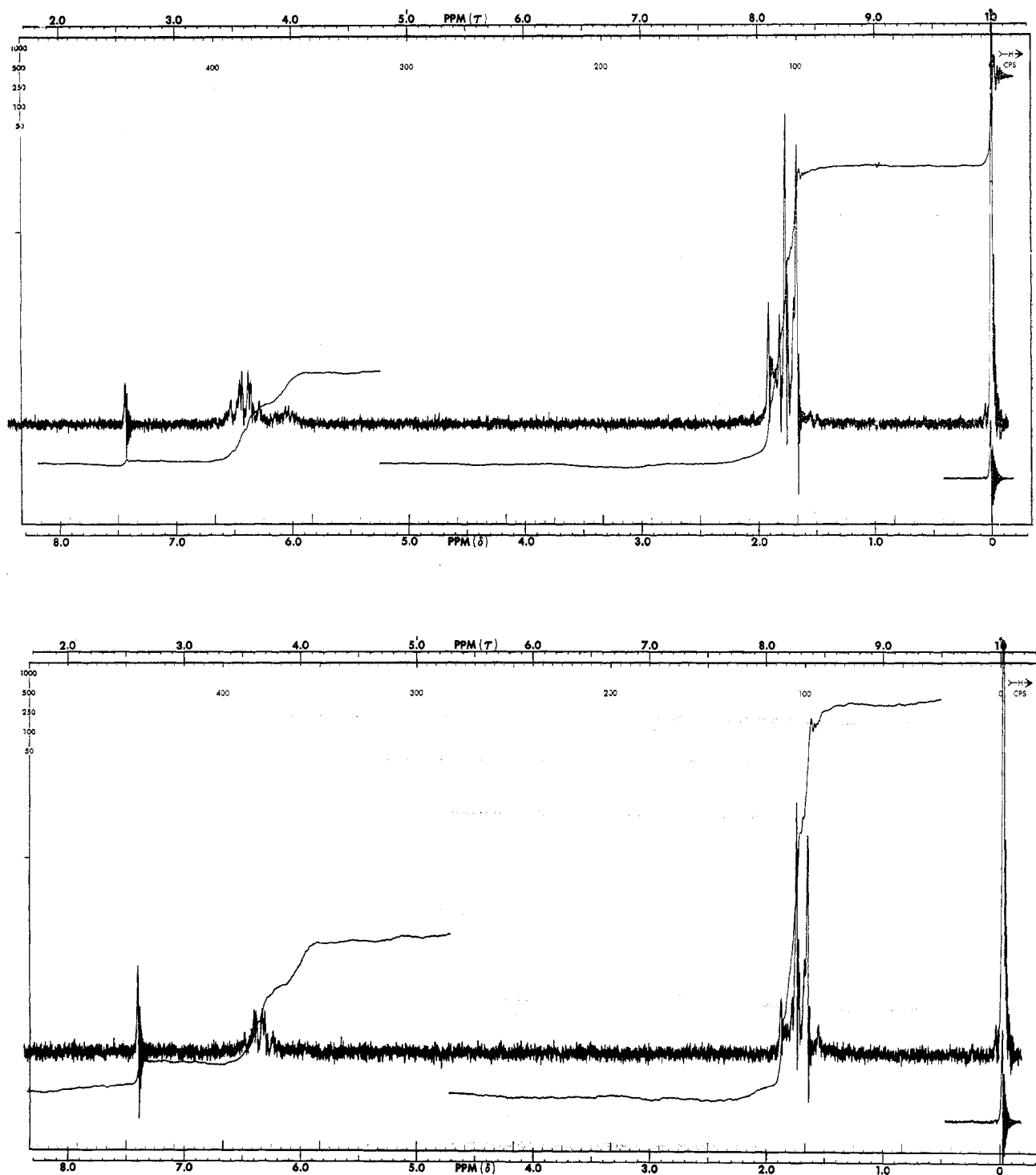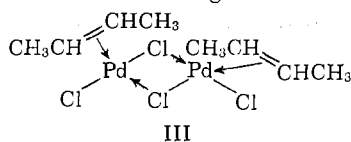(9) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

Figure 2.—Top: pmr spectrum of III.   Bottom: pmr spectrum of IV.

small amounts of butene produced in the early stages of the dimerization. On standing at room temperature III


III

becomes insoluble, presumably by isomerization to the more stable IV.[10] This process can be partially reversed since, if IV is held at 50° in $CHCl_3$ for several hours,

it is slowly converted to III and the solution thus obtained precipitates II on pressuring with ethylene.

A similar *cis–trans* equilibrium has recently been reported for the complex $(C_5H_5)_2Fe_2(CO)_4$.[11] The crystalline compound exists exclusively as the *trans* form but in solution it is largely cisoid.

(10) Professor Baenziger of the University of Iowa is currently studying the structures of these compounds by X-ray crystallography.
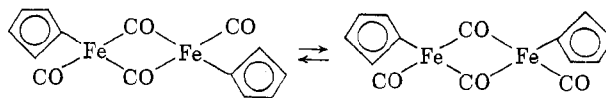
(11) F. A. Cotton, plenary lecture, 9t International Conference on Coordination Chemistry, St. Moritz, Sept 1966.
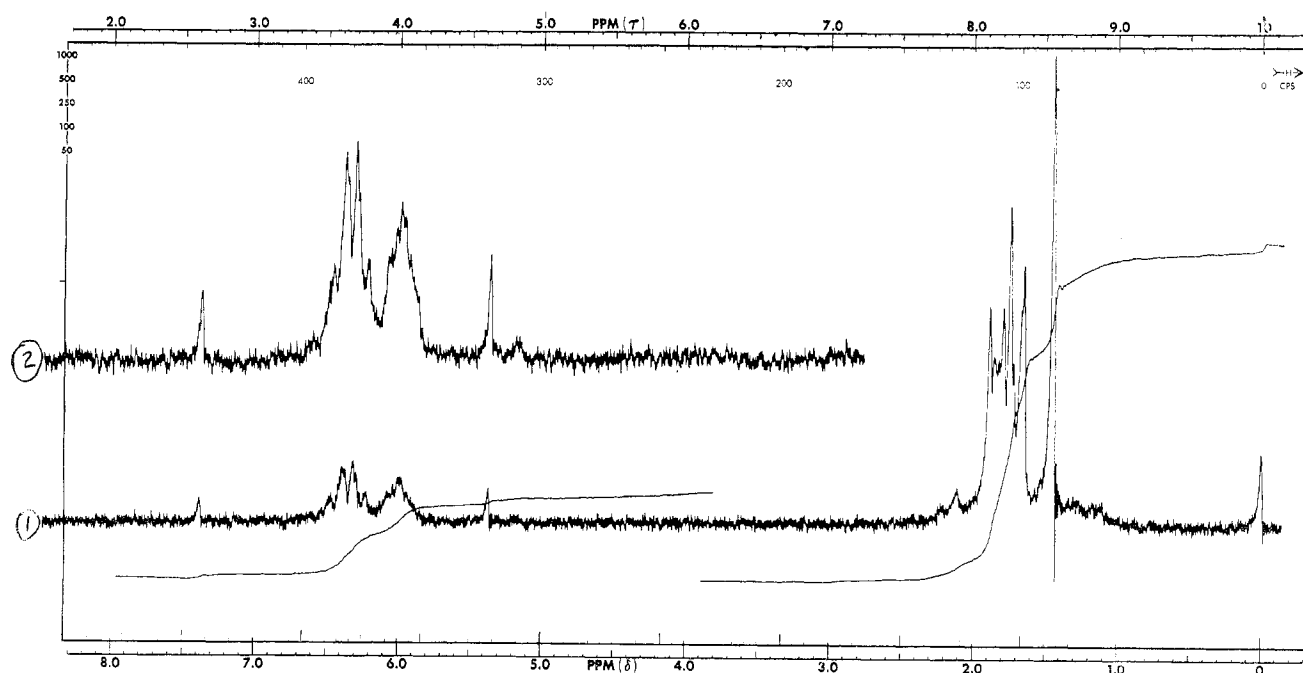
Figure 3.—Pmr spectrum of complex isolated from active solution (compound V).

The interconversion is believed to occur *via* a non-bridged Fe–Fe-bonded species. In this case, the isomerization must occur so rapidly on crystallization that the *cis* form is never isolated as a solid.

Compound II, if kept at −40°, is converted to the soluble catalytic species by ethylene in CHCl₃ free from hydroxylic additives. Since yields of dimer obtained in this way are comparable to those obtained starting with I in ethanol-containing CHCl₃, it appears that the hydroxylic compound only catalyzes the conversion I → II and is not involved in any subsequent reaction of II.

When II is treated with ethylene for 4 hr, it is converted to a solution which has maximum activity in dimerizing ethylene. This solution can be evaporated under vacuum to remove ethylene and butene without loss of activity. The resulting olefin-free solution, when treated at room temperature with a strongly coordinating ligand—for example, benzonitrile—liberates butene with formation of $(C_6H_5CN)_2$-$PdCl_2$. This behavior is typical of an olefin π complex and contrasts with that of π-allyl complexes which are stable to benzonitrile up to 130° and then decompose to give chloralkenes and Pd^0. On concentrating this solution under reduced pressure, a red precipitate is obtained which redissolves in any of the effective reaction media to give a solution which dimerizes ethylene. Compound V, like the parent solution, evolves butene when treated with benzonitrile and is converted to $(C_6H_5CN)PdCl_2$. It has the empirical formula $(C_4H_8)_2$-Pd_2Cl_4. *Anal.* Calcd: C, 20.57; H, 3.43: Cl, 30.53; Pd, 45.47. Found: C, 20.64; H, 3.48; Cl, 30.01; Pd, 45.99. Its pmr spectrum is shown in Figure 3. In all its broad features this spectrum resembles those of III and IV. The infrared spectra of all three compounds are indistinguishable. One is forced to con-
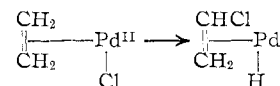
clude that V is yet another isomeric C_4H_8–$PdCl_2$ complex presumably having the structure

$$CH_3CH \diagdown^{CHCH_3Cl} \diagup Cl$$
$$CH_3CH \diagup^{CHCH_3Cl} Pd \diagdown Cl$$

V
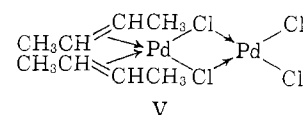
Compound V does not convert, on standing, to the insoluble complex IV. Obviously this would be a more difficult isomerization than III → IV which requires only the rotation of one of the palladium atoms in the dimer. On the basis of these results, we suggest the reaction scheme shown in Scheme I (note that butene is written \=/ for convenience and is not meant to imply a *cis* configuration, and L = solvent or ROH). The detailed mechanism of the step

$$\diagup\diagup^{Cl}_{Pd\diagdown Cl} \longrightarrow \diagup\diagup^{Cl}_{Pd\diagdown Cl}$$

is, of course, far from obvious. Recently, Cramer has discussed a possible mechanism for the isomerization of olefins which involves the formation of palladium hydride complexes as reaction intermediates.[12] These complexes are believed to arise from the reaction

$$CH_2 \quad\quad\quad CHCl$$
$$\|\text{———}Pd^{II} \longrightarrow \|\text{———}Pd$$
$$CH_2 \quad| \quad\quad CH_2 \quad|$$
$$\quad\quad Cl \quad\quad\quad\quad H$$

While such a metal hydride would be a reasonable reaction intermediate in the dimerizations described in this paper, we have obtained no evidence that such an intermediate is, indeed, formed. Analyses of reaction solutions by vpc show no trace of vinyl chloride.

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

SCHEME I
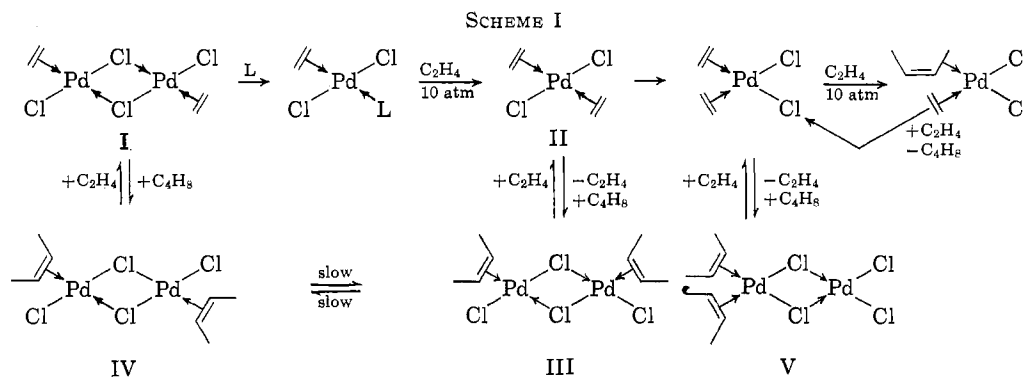
The pmr spectra of concentrated reaction solutions show no high-field signal characteristic of metal hydrides. Addition of sources of hydride to the system (H_2, $NaBH_4$, etc.) inhibit rather than catalyze the reaction. However, the *transient* formation of a Pd–H species
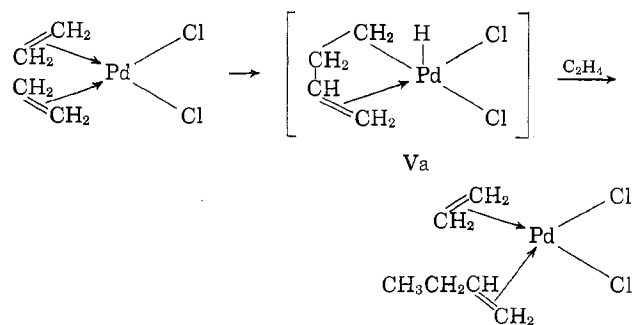
seems to us to be a possible reaction path which requires no external source of hydride. A protonic source of Pd–H seems unlikely also since when anhydrous HCl was added initially to the reaction (HCl: Pd > 1:1 M), the dimerization was markedly inhibited in contrast to the results obtained by Cramer for the $RhCl_3$–CH_3OH system.

The catalyst does not remain active indefinitely and after several days at 40° no more butene is produced. When this solution, after removal of free olefin, is treated with benzonitrile, no butene or other olefin is formed. Instead, upon heating, Pd^0 precipitates quantitatively. It appears probable, therefore, that the active π complex is converted to an inactive π-allyl complex. Addition of excess HCl, which is claimed to convert a π-allyl complex to an olefin π complex,[13] did not reactivate the catalyst.

After the reaction in CH_2Cl_2 had ceased, the solution of inactive catalyst (VI) was concentrated under vacuum. Since this solution was rather viscous and difficult to handle, the complex was precipitated by addition of the solution to cyclohexane. The dark purple solid obtained was dried in a vacuum desiccator. *Anal.* Calcd for $C_{12}H_{21}Pd_2Cl_3$: C, 29.63; H, 4.34; Cl, 21.91; Pd, 43.72. Found: C, 29.88; H, 4.71; Cl, 22.66; Pd, 42.80. This material was unaltered by recrystallization from $CHCl_3$–CCl_4 mixtures and is consequently

assumed to be a single compound. Hydrogenation of VI in CH_2Cl_2 gave a quantitative yield of Pd^0, based on the above empirical formula, HCl, and two organic products with retention times in the vpc corresponding to a branched hexane and a monochlorohexane. The pmr spectrum of VI is shown in Table I. Assignments are based largely upon Statten and Ramey's data for crotylpalladium(II) chloride.[14] The structure which appears to fit the data on the inactive catalyst most satisfactorily is
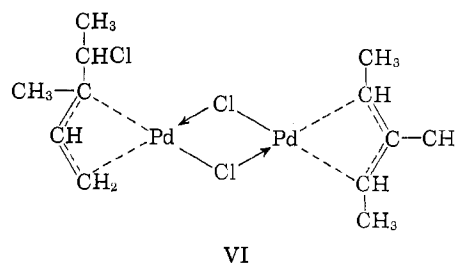
VI

TABLE I

PMR SPECTRUM OF INACTIVE CATALYST
FROM ETHYLENE DIMERIZATION

Chemical shift, τ	Integral	Assignment
4.58 (multiplet)	0.8	H—⟨ ⟩ Pd
5.86 (multiplet)	4.7	H ⟨ ⟩ Pd
6.15 (quartet)	0.8	H—C—Cl
6.88 (multiplet)	0.9	H ⟨ ⟩ Pd
7.89 (singlet)	3.0	CH_3—⟨ ⟩ Pd
8.74 (doublet)	} 12.0	CH_3 ⟨ ⟩ Pd
8.85 (doublet)		CH_3—CH

(13) R. Huttel, *Angew. Chem.*, 456 (1959).

(14) G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

There seem to be two reasonable routes to VI. One involves the assumption that ethylene can remove hydrogen from the active complex VII to give intermediate VIII


VII

IX   VIII
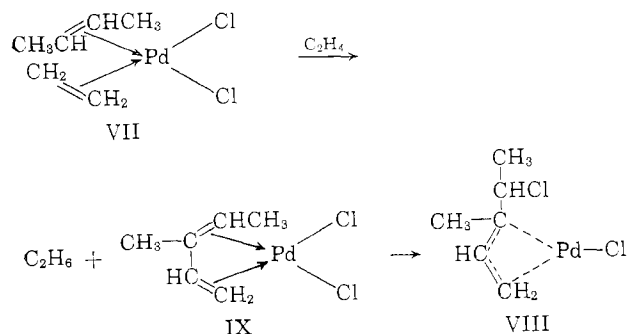
This dehydrogenation step might well occur by reaction of ethylene with an intermediate such as Va, the rate of this reaction being considerably slower than the rate of the reaction which yields dimer. The conversion of intermediates such as IX to VIII is well documented.[15] Attack of VIII upon VII with elimination of HCl could then yield the inactive species VI. An alternative route to compound VII might be attack of traces of acetylene in the ethylene upon VII to yield VIII without the need for postulating a dehydrogenation step.

Some support for the reaction of VII with ethylene to give VIII comes from our observation that the π complex X reacts with a dilute solution of isobutene in chloroform to give the π-allyl complex XI

X

XI
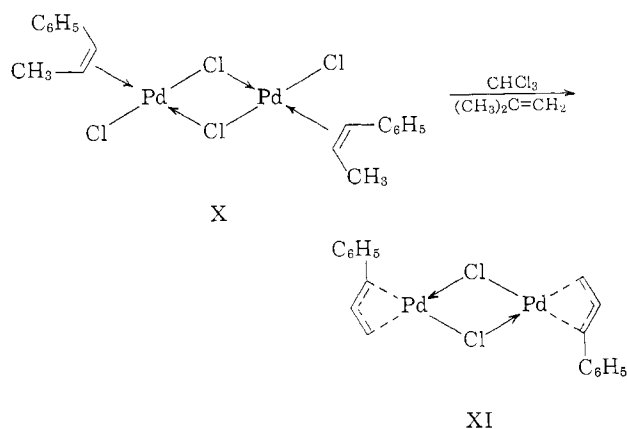
It is significant that addition of hexene to the reaction initially does not decrease the rate of formation of butene. Compound VI cannot be formed, therefore, via a C_6H_{12}–$PdCl_2$ π complex.

Dimerization of Propylene by PdCl₂

Propylene is also dimerized by $PdCl_2$ in those solvents used for the ethylene reaction. $PdCl_2$ propylene complex XII, furthermore, readily forms in CCl_4, C_2H_5Cl, and t-C_4H_9Cl but no dimerization occurs. *Anal.* Calcd for $(C_3H_6)_2Pd_2Cl_4$: C, 16.37; H, 2.74; Cl, 32.47; Pd, 48.42. Found for complex formed in CCl_4: C, 16.41; H, 2.71; Cl, 32.26; Pd, 48.65. Compound XII reacts with 8 atm of propylene at 40° in 2–3

hr to give a clear solution which again appears to contain the active catalyst. This solution, when excess olefin is removed, reacts with benzonitrile to give hexene and $(C_6H_5CN)_2PdCl_2$. After 18 hr, reaction has ceased and the solution now contains a species which reacts with C_6H_5CN at high temperature to give quantitative precipitation of Pd^0. It appears that the formation of an active olefin π complex followed by conversion to an inactive π-allyl species also occurs in the propylene reaction.

In $CHCl_3$ and CH_2Cl_2, $PdCl_2$ yields a product containing ~65% hexene-2 and hexene-3 and ~35% of the isomers of 2-methylpentene and 4-methylpentene. In anisole ~90% linear hexenes are obtained. If $PdCl_2$ is replaced by XII at the start of the reaction, 100% straight-chain hexenes are formed. The branched dimers probably arise by $PdCl_2$ acting as a weak Friedel-Crafts catalyst.

Reaction of Butenes and Higher Olefins

No evidence for dimerization of butene or the higher olefins was found with these systems. The initial formation of a complex $(C_4H_8)_2Pd_2Cl_4$ readily occurs from either 1-butene or *cis*- and *trans*-2-butene. These complexes have identical infrared and pmr spectra. Since all of the olefins are rapidly isomerized to a common isomeric mixture by $PdCl_2$, the product probably consists of a common mixture of $PdCl_2$–C_4H_8 complexes. The initially formed complex is not transformed to a species $(C_4H_8)_2PdCl_2$ and appears unchanged after several days in the presence of excess butene.

Other Palladium Salts

Palladium fluoride, bromide, iodide, and nitrate gave only traces of dimer in these systems. No complexes of structure $(C_2H_4)_2Pd_2X_4$ were observed, and there appeared to be little, if any, reaction between the ethylene and these salts. Attempts to prepare $(C_6H_5CN)_2PdF_2$ as a precursor for the synthesis of $(C_2H_4)_2Pd_2F_4$ by the Kharasch method were unsuccessful.

Palladium cyanide in CH_2Cl_2 dimerized ethylene at about half the rate of $PdCl_2$ under the same conditions. The $Pd(CN)_2$ was coated with a white solid during the reaction. This proved to be polyethylene which, from the ratio of the infrared bands at 730 and 1305 cm⁻¹, was highly crystalline.[16] Polyethylene of lower molecular weight was isolated from the CH_2Cl_2 solution by precipitation with methanol. This reaction has recently been reported elsewhere.[17] Propylene with $Pd(CN)_2$ in CH_2Cl_2 gives low molecular weight polypropylene. No reaction was observed with butene.

Dimerization of Ethylene and Propylene by Rhodium Chloride

Dimerization of Ethylene.—When a suspension of 1 g of rhodium trichloride trihydrate in 100 ml of chloroform was treated with ethylene (10 atm) at 25° for

(15) M. Donati and F. Conti, *Tetrahedron Letters*, 1219 (1966).

(16) A. Renfrew and P. Morgan, Ed., "Polythene," Interscience Publishers, Inc., New York, N. Y., 1957.

(17) A. U. Blackham, U. S. Patent 3,194,800 to National Distillers and Chemical Corp. (1936).

5.5 hr, 48 g of butene (almost exclusively butene-2 with *trans/cis* = 2.6) was produced along with a trace of hexene (0.2 g).

The reaction is faster in chloroform than in carbon tetrachloride and even proceeds in the absence of solvent, but only very slowly (5 g of butene in 8 days). In water, no reaction occurs, while in water–methanol or water–dioxane, μ-dichloro-tetraethylenedirhodium(I) is formed. This complex is inactive under our conditions for the dimerization of ethylene.

Water of hydration is an effective agent for increasing the catalytic activity of rhodium trichloride. The rate of dimerization of ethylene is at least 20 times faster with the trihydrate than with anhydrous rhodium trichloride.

Dimerization of Propylene.—Rhodium trichloride trihydrate in a wide range of reaction media catalyzes the dimerization of propylene to a mixture of 2-methyl-pentenes and *n*-hexenes. The amounts of branched- and straight-chain isomers were 57 and 43%, respectively, as shown by hydrogenation to 2-methylpentane and *n*-hexane. Conversions were from 6 to 33%. The product distribution was the same in chloroform, nitrobenzene, and ethanol. Addition of HCl increased the rates but did not increase the conversions. The observations that the reaction is acid catalyzed, is unaffected by a large excess of ethanol, and gives predominantly branched-chain isomers of hexene suggest that the mechanism of the reaction catalyzed by rhodium chloride is completely different from that of the palladium chloride reaction. It seems likely that an insertion reaction on a rhodium–alkyl bond, demonstrated by Cramer in methanol, occurs in all reaction media.

Experimental Section

(1) All reactions were carried out in 6-oz Fischer–Porter aerosol compatibility tubes immersed in a constant-temperature bath and magnetically stirred. In typical runs, 100 ml of reaction medium, 1 g of $PdCl_2$, and 150 psi of ethylene pressure were used.

Reagents were purified by distillation through a 1-m spinning-band column if vpc showed them to be impure. They were dried conventionally with magnesium sulfate or molecular sieves.

Normally, reactions were carried out by weighing reagents into a dried Fischer–Porter tube under a flow of argon after which the tube was connected to a manifold under ethylene or propylene pressure. In some runs, all operations were conducted under argon in a steel drybox; however, these more extreme procedures aimed at excluding trace moisture appeared to have no measurable effect on our results.

Initially, butene yields were measured by distilling the reaction mixture into a Dry Ice trap. In later runs, the increase in liquid level in the reactor was used, this being calibrated against known weights of butene. However, low conversions were measured by vpc using a di-2-ethylhexyl sebacate column in a Perkin-Elmer 154 instrument at 30°. Analysis of the butene isomer distribution was carried out on a diisodecyl phthalate column at 30° or on a silver nitrate–diethylene glycol column at room temperature.

Hexene yields from propene dimerization were measured either by isolating the product on a spinning-band column or by calculating from quantitative vpc work using a 10% SE-30 on 80–100S column in an F & M 810 instrument or with a 10^1 column 75% FFAP on 70–80 mesh Chromosorb G in a Wilkens Aerograph A-350-B. Ratios of branched to linear hexenes were analyzed by reducing the olefins with a Brown[2] hydrogenator and then analyzing the resultant mixture of *n*-hexane and 2-methylpentane by vpc on either a silver nitrate–diethylene glycol column in a Perkin-Elmer 154 or a 5% FAAP on 70–80 mesh Chromosorb G column (10^1) in an F & M 810.

(2) For the isolation of complex II, the reaction vessel containing II under ethylene pressure was cooled to −40°. Ethylene pressure was removed and the suspension of II introduced through the ball-joint of the apparatus in Figure 1 while a stream of argon was introduced at A. The whole apparatus was kept at −40 to −80°. Stopcock C was then closed and vacuum applied at B. Compound II was collected on filter disk D and dried by the argon flow. Stopcocks A and B were closed, C was connected to a gas collection apparatus, and then the low-temperature bath was removed. Stopcock C was opened and the system was left undisturbed until gas evolution ceased. The volume of collected gas was measured and a sample was analyzed by vpc and mass spectrometry. Blank measurements to compensate for volume increase due to expansion of the gas between −40° and room temperature were made. The ethylene–palladium chloride complex remaining was removed from the filter and weighed.

(3) The pmr spectra of III, IV, and V were obtained in CCl_4 at 25° on a Varian A-60A instrument. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.