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Study of Hydrogenation of Olefins Catalyzed by Polymer-Bound Palladium (II) Complexes

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A polymer-bound palladium (II) chloride complex has been prepared by the reaction of palladium chloride with a phosphinated polystyrene. Under mild conditions the polymer palladium complex catalyzes the hydrogenation of alkenes and alkynes, particularly the selective hydrogenation of conjugated dienes to monoenes. The catalytic activity for a variety of substrates decreases in the following order: conjugated dienes > nonconjugated dienes > terminal olefins > internal olefins. Oxygen-containing solvents remarkably promote the catalytic activity of the palladium complex. The rates of hydrogenation of cyclohexene, styrene, and 1,3-cyclooctadiene have been studied and the dependence on factors such as substrate concentration, catalyst concentration, pressure, and temperature has been determined. The data can be accommodated by rate expressions of the form: rate $= k_1k_2[S][H_2][A]/(k_{-1} + k_1[S] + k_2[H_2])$ for cyclohexene, and rate $= k_2[H_2][A]$ for styrene and 1,3-cyclooctadiene, where $[S]$ and $[A]$ are the olefin and catalyst concentrations, respectively, and $[H_2]$ is the concentration of hydrogen in solution. A mechanism for hydrogenation is proposed on the basis of the kinetic studies. It is revealed that the reactivities of the polymer palladium complex catalyst and of an analogous catalyst system $PdCl_2(PPh_3)_2$–$SnCl_2$ reflect the electronic state and the coordination number of the complexes.

INTRODUCTION

Heterogeneous reactions with metal catalysts have been studied extensively, however, the design of the catalysts is not easy because the active sites of the catalysts are not well-defined. Only a small portion of the metals is available and effective. On the other hand, homogeneous complex catalysts have well-defined active sites, and consequently the steric and electronic environments of the metal atom can, at least in principle, be varied easily. Most of the metal is available for catalysis. But the homogeneous catalysts have so far been used only in limited chemical processes because of many practical problems including corrosion, deposition of the catalysts on the wall of the reactor, and recovery of the catalysts from the reaction mixture. In order to combine the advantages of both homogeneous and heterogeneous catalysts, methods for chemically bonding metal complexes to an insoluble organic or inorganic polymer have been developed in recent years (*1*, *2*). The catalysts, prepared in such a manner, are situated between those usually classified as "heterogeneous" and those classified as "homogeneous," and can be regarded as a new class of catalysts. Therefore, it is

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interesting to study the mechanism of the heterogeneous reaction using the new catalysts and to discuss their reactivities for many organic reactions, compared with those of analogous homogeneous catalysts.

Bruner and Bailar have prepared styrene–divinylbenzene copolymer-bound palladium (II) chloride, which they used in the hydrogenation of soybean methyl esters (*3*). They have described the major differences between the catalytic properties of the polymer complex and those of an analogous homogeneous complex, $PdCl_2(PPh_3)_2$. The polymer complex catalysts are much more active for hydrogenation than the homogeneous catalyst, and the polymer catalyst hydrogenated conjugated dienes at a faster rate than nonconjugated dienes, contrary to the homogeneous system. However, a detailed mechanistic study has not been done. In addition, the homogeneous catalyst does not display enough activity to permit a detailed kinetic study (*4*).

Previously we have prepared a polymer-bound palladium (II) chloride complex from the reaction of $PdCl_2$ and phosphinated polystyrene, and found that the polymer complex had catalytic activity for hydrogenation (*5*), codimerization of acetylenes and olefins (*6*), and codimerization of styrene and olefiins (*7*). In this paper, we report studies of the detailed characterization of the polymer–palladium complex and of the mechanism of olefin hydrogenation on the basis of the kinetic study. A mechanism is proposed which involves the heterolytic fission of hydrogen, forming a Pd^{II}–H species. Furthermore, it is revealed that the catalytic properties of both the polymer complex and an analogous homogeneous complex reflect the electronic state and the coordination number of the complexes.

EXPERIMENTAL

Gas–liquid chromatography (glc) measurements were made using a Shimadzu GC-4BPF chromatograph with a flame ionization detector and 3-m columns of Apiezon grease L on Neopack 1A or bis[2-(2-methoxyethoxy)-ethyl]ether on Chromosorb P. Infrared spectra were measured with an Hitachi EPI-G spectrometer. XPS spectra were taken on an Hitachi 507 photoelectron spectrometer using AlK_α radiation.

Materials

Hydrogen was passed through an Engelhard Deoxo catalyst tube and through a calcium chloride drying tube before admission to the vacuum system. Deuterium gas supplied by Takachiho Kagaku Cogyo K. K. was used without purification. All solvents were dried and distilled under nitrogen. All unsaturated compounds were dried and purified by distillation or recrystallization under nitrogen. The palladium chloride was from Wako Pure Chemical Industries, Ltd. Dichlorobisbenzonitrilepalladium (II), $PdCl_2(PhCN)_2$ (*8*), and dichlorobis(triphenylphosphine)-palladium (II), $PdCl_2(PPh_3)_2$ (*4*), were prepared by reported procedures. A polystyrene powder (no cross-linking, 2000–3000 molecular weight) was chloromethylated on 100% of the aromatic rings by the method of Pepper *et al.* (*9*). The chloromethylated polystyrene was diphenylphosphinated by the method of Grubbs and Kroll (*10*). Table 1 presents the analytical data for two preparations of the phosphinated

TABLE 1

Analytical Data of the Diphenylphosphinated Polystyrene Ligands[a]

Resin	Percentage			
	C	H	P	Cl
P-1	82.15	6.06	10.48	0.0
P-2	82.42	6.25	8.71	0.54

[a] $(C_{21}H_{19}P)_n$ requires: C, 83.41; H, 6.36; P, 10.24%.

polymer (P-1 and P-2). The Bailar type of polymer-bound palladium complex was prepared as follows (*3*). Under a nitrogen atmosphere, 0.495 g of P-1 was suspended for 20 hr in 100 ml of a refluxing acetone solution containing 0.338 g of dichlorobisbenzonitrilepalladium (II). The yellow product was recovered by filtration, washed with acetone and ether, and dried under vacuum (*3*). Found: C, 54.22; H, 3.98; Cl, 11.17; N, 0.00; P, 7.77%.

Preparation of Polymer-Bound Palladium Complex

All of the polymer-bound palladium complexes were prepared in approximately the same manner. The synthesis of PC-2 is typical. Under a nitrogen atmosphere, 2.5 g of P-1 (P, 8.5 mmol) was dissolved for 26 hr in 100 ml of a refluxing benzene–ethanol (1:2) solution containing 1.5 g of palladium chloride (II) (8.5 mmol). The yellow product was precipitated. The product was recovered by filtration and washed with ethanol until the filtrate was colorless. The solid was dried for 50 hr under vacuum. The analytical data for the various preparations of the polymer complexes are summarized in Table 2.

Instruments and Hydrogenation Procedure

The reaction vessel was a 25-ml flask with a sidearm packed with silicone rubber. It was attached to a reaction system with a manometer, a gas buret, and a vent, and was set in a water bath on a magnetic stirrer which was maintained at a constant temperature. The polymer catalyst was weighed into the reaction vessel and the vessel was attached to the reaction system. The system was evacuated and flushed five times with hydrogen. A solvent was added and the mixture was stirred for 30 min. The stirring was then stopped and a substrate was introduced. Hydrogenation was started, with stirring of the mixture anew. The standard solvent in kinetic runs was benzene–ethanol (1:1) [(13 − n) ml], where n is the volume of substrate used. The stirring was done so rapidly that a reaction rate did not depend on the stirring rate. The volume of hydrogen uptake at atmospheric pressure or pressure change of hydrogen in a closed system was measured. Samples were withdrawn from the reaction mixture at regular time intervals and were analyzed by gas chromatography. PC-4 catalyst was used in kinetic runs and PC-2 in other runs, unless otherwise noted.

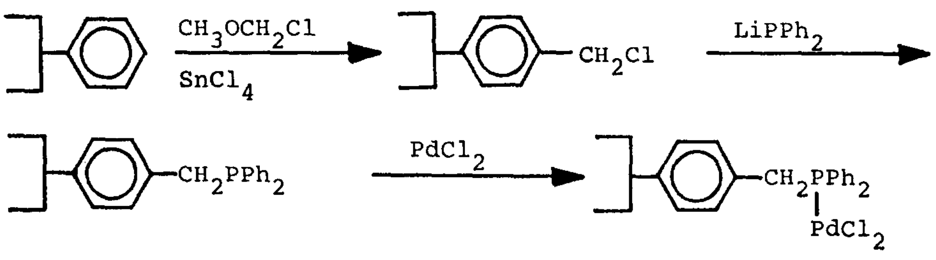
Deuteration of Dimethyl Fumarate and Dimethyl Maleate

To 5 ml of tetrahydrofuran containing 0.02 g of PC-2 was added 0.40 g of the ester. Deuterium gas was admitted. After complete absorption of deuterium the solution was filtered and concentrated under vacuum. The infrared spectra of the succinates obtained were measured in neat.

RESULTS AND DISCUSSIONS

Preparation of Polymer-Bound Palladium Complex

The polymer-bound complex was prepared as shown below.



SCHEME I

Polystyrene with no cross-linking was chloromethylated (*9*), followed by phosphination (*10*) to give diphenylphosphinated resin. A 100% phosphinated resin (P-1) and a 74% phosphinated resin (P-2) were employed. The polymer-bound palladium complexes were prepared by the bridge-splitting reaction method. An equimolar mixture of palladium chloride (II) and the phosphinated resin as phosporus in benzene–ethanol was refluxed to give a yellow complex. In the solution of pure ethanol, palladium black deposited slightly during the reaction. The phosphinated resin dissolved in solvents such as benzene, tetrahydrofuran, and dioxane since the resin was not cross-linked. The polymer-bound complexes obtained, however, did not dissolve in all the solvents used in this study. This indicates that the polymer chains may be cross-linked with just a small portion of palladium atoms.

The analytical data for the complexes are summarized in Table 2. The palladium analysis was obtained in the case of PC-2. The atomic ratio of phosphorus to palladium was near one in all the complexes prepared under various conditions. This result shows that each palladium atom can be attached to only one phosphorus atom on the polystyrene, that is, the polymer chain is not so flexible, as adjacent phosphorus atoms can readily coordinate to one palladium atom, while many authors suppose that two phosphorus atoms on the polystyrene form a chelate ring to each metal atom (*1*). The atomic ratio of chlorine was almost two.

TABLE 2

Analytical Data of the Polymer-Bound Palladium Complexes

Complex	Resin used	Percentage				Empirical atomic ratio P/Pd
		C	H	Cl	P	
PC-1	P-1	61.17	4.54	9.20	6.68	1.23[c]
PC-2	P-1	53.88	4.04	12.48	7.62	1.17[b]
PC-2[a]	P-1	53.97	4.01	12.11	7.29	1.10[c]
PC-3	P-1	53.88	4.36	11.76	6.55	0.97[c]
PC-4	P-2	56.05	4.33	11.83	6.39	1.04[c]

[a] Recovered complex after olefin hydrogenation.

[b] Pd analysis was obtained on this complex: observed, 22.0%.

[c] Pd content was calculated by difference.

TABLE 3

Palladium 3*d* and Chlorine 2*p* Binding Energies (eV)[a]

Compound	Pd		Cl 2*p*
	$3d_{3/2}$	$3d_{5/2}$	
Ⓟ –$PdCl_2$	344.0	338.6	199.1
Ⓟ –$PdCl_2$[b]	343.8	338.5	199.2
Bailar's (*1*)	343.5	338.2	198.8
$PdCl_2(PPh_3)_2$	343.6	338.3	198.6
$PdCl_3$	343.6	338.1	199.3

[a] The binding energy values are referenced to carbon 1*s* (285.0 eV), and the energy differences were determined with an accuracy of ±0.2 eV.

[b] Recovered complex after olefin hydrogenation.

Infrared Studies

The infrared spectrum of the polymer complex in a KBr disk contained one band not found in the spectrum of the polymer ligand. This band appeared at 351 cm^{-1}. The terminal *trans* palladium–chloride stretching band in several compounds of the general form $PdCl_2P_2$ (P is a tertiary phosphine or arsine) appears at 350 to 360 cm^{-1} (*11*). The polymer complex appears to exist exclusively in the *trans* configuration. In addition, the infrared spectrum of the recovered complex did not vary after olefin hydrogenation.

X-Ray Photoelectron Spectroscopy Studies

According to elemental analysis and infrared absorption spectroscopy, the oxidation state of the polymer–palladium complex seems to be divalent. Furthermore, the electronic state was examined by use of the XPS technique

The palladium 3*d* and chlorine 2*p* electron binding energies were measured for the polymer–palladium complexes and other compounds (Table 3). The palladium 3*d* spectrum of the polymer complex is shown in Fig. 1. The palladium $3d_{5/2}$

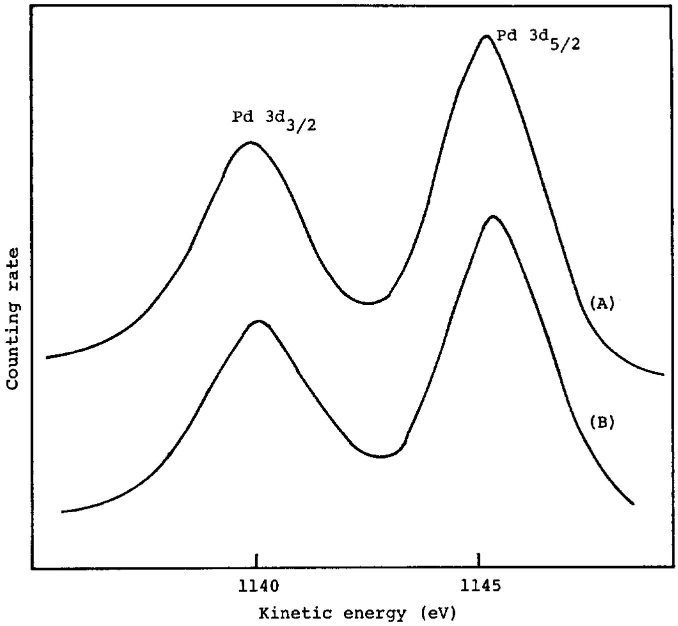


FIG. 1. Palladium 3*d* XPS spectra of polymer-bound palladium complex (A) and the recovered complex after olefin hydrogenation (B).

peak has full width at half-maximum ca. 2.9 eV and no shoulders. The Pd (3*d*) binding energies of the polymer complex are slightly higher than those of other divalent compounds and the Cl (2*p*) binding energy is higher than that of $PdCl_2(PPh_3)_2$ with a terminal Pd–Cl bond. The electronic state of Pd–Cl bond moieties in the polymer complex as a whole is of lower electron density, and the electrons on palladium and chlorine atoms may flow into the polymer ligand. The XPS spectra of the recovered complex did not vary appreciably after hydrogenation. In addition, the polymer–palladium complexes did not show an electron spin resonance (ESR) signal due to monovalent palladium species.

From the results of elemental analysis, ir spectroscopy, and XPS, the most likely structure of the polymer complex seems to be a three-coordinated Ⓟ $-Pd^{II}-Cl_2$ (Ⓟ is the polymer ligand). Interestingly, this structure is similar to that of a polymer-bound divalent rhodium complex prepared by a reaction of rhodium trichloride (III) with the same resin (P-1) as above (*12*).

It is noteworthy that the polymer ligand stabilizes the coordinatively unsaturated complex since the adjacent phosphine moieties block the vacant coordination sites.

Catalytic Hydrogenation of Olefins and Acetylenes

In a variety of solvents, the polymer–palladium complexes are extremely efficient catalysts for the heterogeneous hydrogenation of alkenes and alkynes at ambient temperature and pressure of 1 atm or below. Functional groups such as keto-, hydroxy-, cyano-, nitro-, ether, ester, or carboxylic acid are not hydrogenated under the reaction conditions. The rate of gas uptake attained the maximum within about 1 min. With pretreatment of the catalyst with hydrogen in the presence of a solvent, the induction period disappeared. Therefore, all reactions were started after pretreatment with hydrogen in the presence of a solvent for 30 min.

Table 4 summarizes the initial rates of hydrogen uptake for the hydrogenation of olefins and acetylenes with the polymer complex. The polymer catalyst displays a high activity for the hydrogenation of styrene, isoprene, 1,3-cyclooctadiene, and allyl compounds. They are conjugated compounds or can be isomerized to conjugated compounds with a carbon–carbon double bond or carbon–oxygen double bond. The activity is very sensitive to the steric hindrance about the carbon–carbon double bond and to the molecular size of substrates, particularly in the case of cyclic olefins.

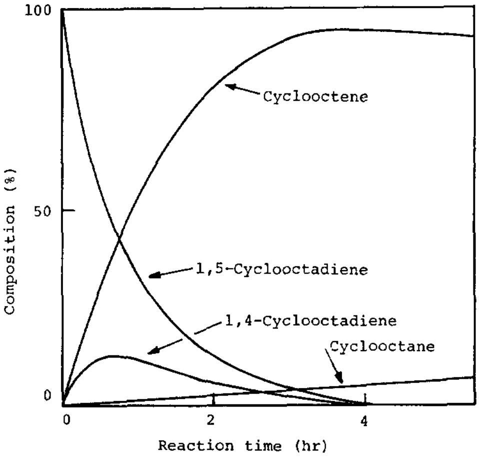


FIG. 2. Hydrogenation of 1,5-cyclooctadiene in benzene–ethanol (1:1) under 1 atm of hydrogen at 25°C.

The double bonds of nonconjugated dienes and external olefins migrated to give conjugated dienes and internal olefins, respectively, in the course of the hydrogenation, as shown in both Figs. 2 and 3. In the case of the hydrogenation of 1,5-cyclooctadiene, 1,3-cyclooctadiene was not detected because the rate of hydrogenation of 1,3-cyclooctadiene is much higher than that of isomerization of 1,4-cyclooctadiene to 1,3-cyclooctadiene. As shown in Fig. 3, 1-heptene was isomerized to internal olefins at a faster rate than it was hydrogenated. The hydrogenation of allylbenzene was found to proceed through β-methylstyrene. Allyl alcohol was also isomerized to propionaldehyde and the rate of the formation of propionaldehyde was higher than that of propyl alcohol. These results show that the rate of double-bond migration is higher than that of the hydrogenation of

TABLE 4

Hydrogenation Rates of Olefins and Acetylenes[a]

Substrate	Initial rate (ml/min)
Styrene	8.10
1-Heptene	3.94
2-Heptene	0.59
1-Dodecene	2.83
Cyclohexene	0.84
Cyclooctene	0.07
Allyl alcohol	5.72
Allybenzene	5.10
Allyl chloride	2.52
Acrolein	1.90
Methyl acrylate	5.60
1,5-Cyclooctadiene	0.93
1,3-Cyclooctadiene	5.26
Isoprene	9.60
1-Hexyne	2.98
Phenylacetylene	3.53

[a] Using polymer catalyst; 3.19×10^{-3} mol/liter of substrate; 0.335 mol/liter, 1 atm of hydrogen at 25°C in [13 − (volume of substrate)] milliliters of benzene–ethanol (1:1).

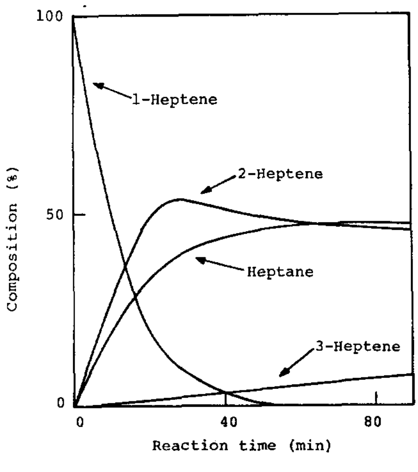


FIG. 3. Hydrogenation of 1-heptene in benzene–ethanol (1:1) under 1 atm of hydrogen at 25°C.

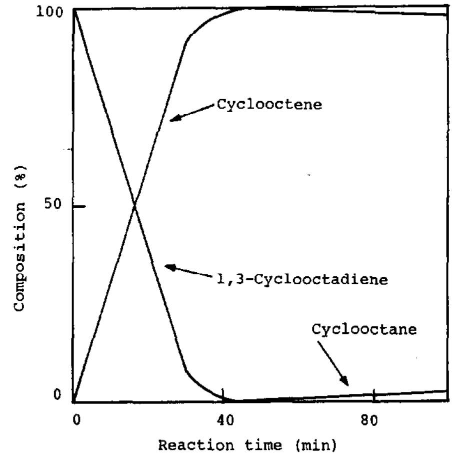


FIG. 4. Hydrogenation of 1,3-cyclooctadiene in benzene–ethanol (1:1) under 1 atm of hydrogen at 25°C.

isolated double bonds. Therefore, nonconjugated dienes are mainly hydrogenated after isomerization to conjugated dienes. The isomerization was not observed in the absence of hydrogen under the reaction conditions used. Dienes were selectively hydrogenated to monoenes, as shown in both Figs. 2 and 4. Conjugated dienes were hydrogenated more rapidly and selectively to monoenes than nonconjugated dienes.

Isoprene was selectively hydrogenated to monoenes and the monoenes were not hydrogenated to isopentane in the presence of the unreacted isoprene (Fig. 5). The results show that the isomerizations of the monoenes did not occur in the presence of the unreacted isoprene since hydrogenation and isomerization are catalyzed by the same palladium–hydride species (mentioned later). Therefore, hydrogenation can be used to determine whether the addition of hydrogen to conjugated dienes is the 1,2- and/or 1,4-type. The ratio of the 1,2- and the 1,4-addition was about 1:1 as judged by comparison of the rate of formation of 2-methyl-1-butene and 3-methyl-1-butene produced by the former with that of 2-methyl-2-butene produced by the latter. This suggests that the half-hydrogenated state contains a π-allylic intermediate.

The reactivity of the polymer catalyst for the hydrogenation of unsaturated compounds is discussed in detail later in connection with the reaction mechanism.

Table 5 summarizes the results of the hydrogenation of styrene in a variety of solvents. The polymer catalyst displayed a high activity for hydrogenation in oxygen-containing solvents such as dimethyl formamide, ethyl alcohol, tetrahydrofuran, and acetone. These solvents solvate the catalyst species to cause an irreversible yellow-to-green color change in the cata-

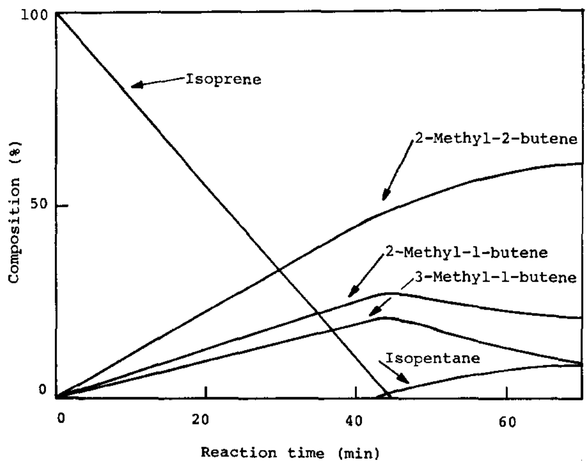


FIG. 5. Hydrogenation of isoprene in benzene–ethanol (1:1) under 1 atm of hydrogen at 25°C.

TABLE 5

Effect of Solvent on Styrene Hydrogenation[a]

Solvent	Initial rate (ml/min)
Dimethyl formamide	8.04
Ethanol	7.74
Tetrahydrofuran	6.13
Acetone	6.10
Benzene	2.84
Chloroform	2.45
Ethyl acetate	2.08
Methylene chloride	1.68
Acetic acid	1.45
Cyclohexane	0.22
Nitromethane	0.10
Dimethyl sulfoxide	0.09

[a] Using polymer catalyst; 3.19×10^{-3} mol/liter of styrene; 0.67 mol/liter, 1 atm of hydrogen in 12 ml of solvent at 25°C.

lyst. Presumably, the coordination of oxygen atoms to palladium plays an important role in accelerating the catalytic activity. Dimethyl sulfoxide and nitromethane, however, decreased the rate of hydrogenation. They coordinate much more strongly to palladium and disturb the coordination of hydrogen or an olefin to the metal. Ethyl alcohol, which is a poor swelling solvent for polystyrene, seems to display a lower activity for hydrogenation than better swelling solvents such as benzene, acetone, and ethylacetate (*13*),[2] since contraction of the polymer decreases the diffusion rate of a substrate into polymer channels. In our hydrogenation, however, ethanol displayed a higher activity than the better swelling solvents (*13*). This fact suggests that the contraction does not have much effect on the rate. Although the yellow complex has the same elemental analysis, infrared spectrum, and XPS spectrum as the green one, the yellow complex displayed a lower activity than the green one. At the present stage, no further explanation can be given for this phenomenon.

Quantitative Measurements

The overall rates of hydrogenation of cyclohexene, styrene, and 1,3-cyclooctadiene have been measured and the dependence on catalyst concentration, hydrogen pressure, substrate concentration, and temperature has been investigated. Benzene–ethanol (1:1) was used as a solvent in order to swell the polymer catalyst and increase the activity. The rate of hydrogen uptake was obtained from the tangent to the plot of hydrogen uptake against time under atmospheric pressure or to the plot of hydrogen pressure against time in a closed system. The conversion to the rate of consumption of substrate (S) (mol liter^{-1} sec^{-1}) was made using the stoichiometric relationship $-d[H_2]/dt = -d[S]/dt$. The hydrogenation products of cyclohexene, styrene, and 1,3-cyclooctadiene are cyclohexane, ethylbenzene, and cyclooctene, respectively

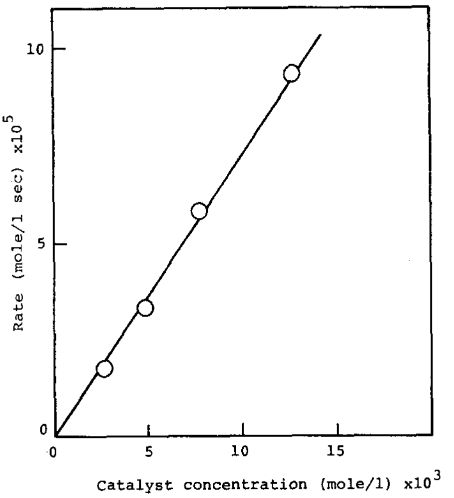


FIG. 6. Dependence of rate of hydrogenation of cyclohexene on catalyst concentration with 0.374 M cyclohexene at 25°C.

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[2] Regen (*13*) used 2% cross-linked polymer beads, whereas we used no cross-linked polymers. The influence of solvent on the degree of swelling of the latter seems to resemble that of the former.

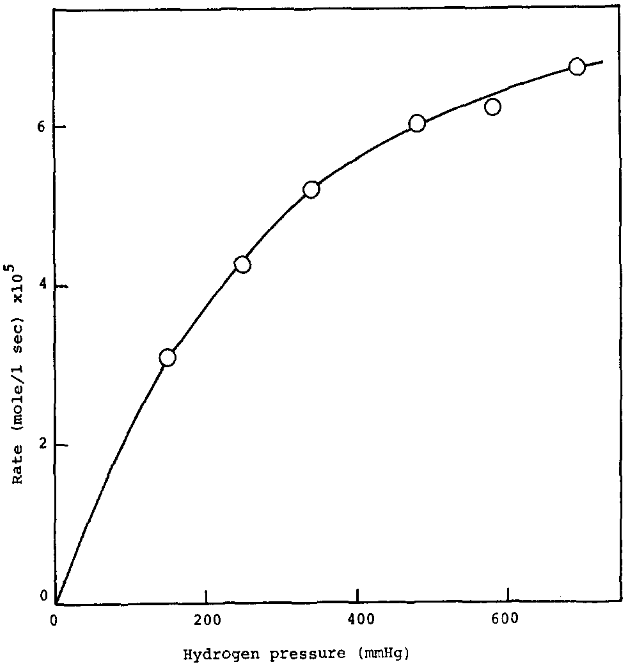


FIG. 7. Dependence of rate of hydrogenation of cyclohexene on hydrogen pressure with 4.95 mM catalyst and 1.12 M cyclohexene at 25°C.

Hydrogenation of Cyclohexene

A plot of the rate of hydrogen consumption against catalyst concentration is shown in Fig. 6. The rate increases linearly with increasing catalyst concentration. This indicates that the mass-transfer effect could be neglected in the reaction conditions.

A typical plot showing the rate of hydrogen uptake against hydrogen pressure is shown in Fig. 7. The rate does not increase linearly with increasing hydrogen pressure, but approaches an asymptotic value. The plot of the reciprocal of this rate against the reciprocal of the hydrogen pressure (Fig. 8) is linear, with a positive intercept of the y axis.

The qualitative dependence of the rate on substrate concentration ($[S]$ mol liter^{-1}) can be seen from Fig. 9. From results under standard conditions, the reciprocal of the rate against the reciprocal of the cyclohexene concentration is a linear plot with a positive intercept on the y axis (Fig. 10).

Rates were measured at three temperatures between 0 and 25°C for various cyclohexene concentrations. From the plots of the reciprocal of the rate against the reciprocal of the olefin concentration, which remain linear throughout the temperature range, the intercepts on the y axis given in Table 6 can be obtained, and rate constant derived from them are given as discussed later.

Hydrogenation of Styrene and 1,3-Cyclooctadiene

A plot of the rate of hydrogen consumption against catalyst concentration is shown in Fig. 11. The rates of styrene and 1,3-cyclooctadiene increase linearly with increasing catalyst concentration.

A plot of the rate against hydrogen pressure is shown in Fig. 12. Both the rates increase linearly with increasing hydrogen pressure.

The qualitative dependence of the rate on substrate concentration can be seen

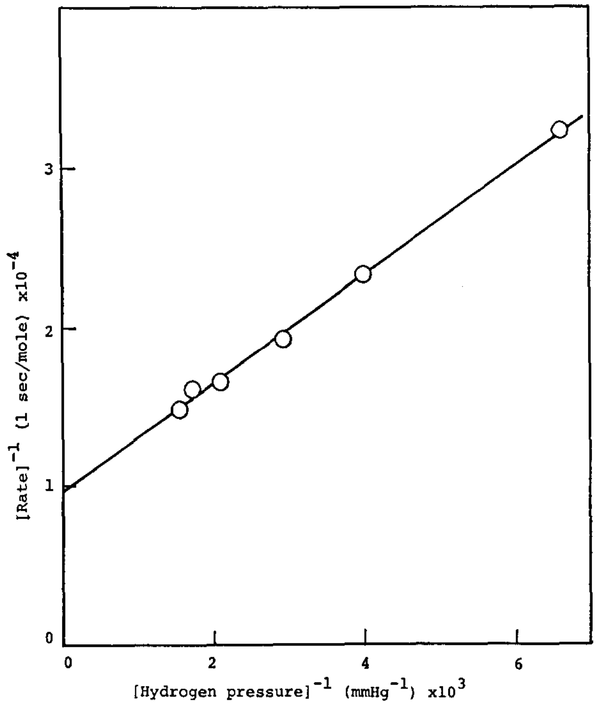


FIG. 8. Plot of the reciprocal of rate of hydrogenation of cyclohexene against the reciprocal of hydrogen pressure.

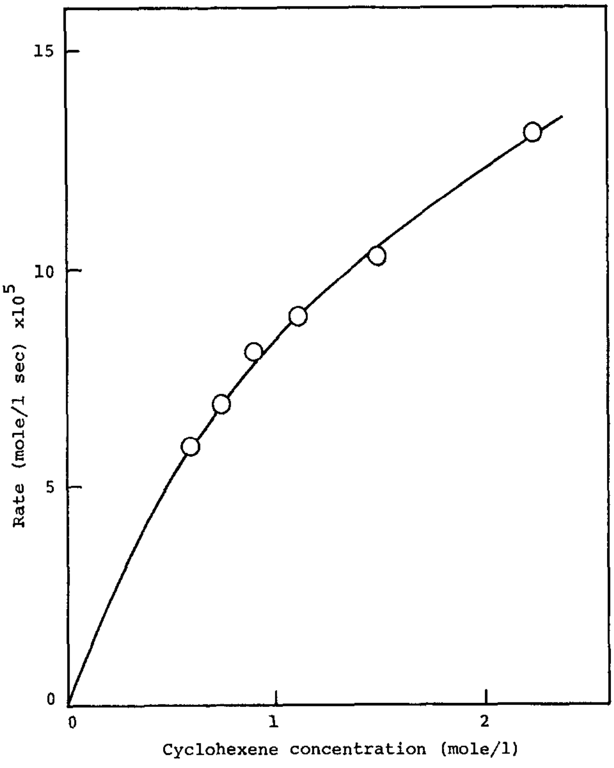


FIG. 9. Dependence of rate of hydrogenation of cyclohexene on the olefin concentration with 4.95 m*M* catalyst at 25°C.

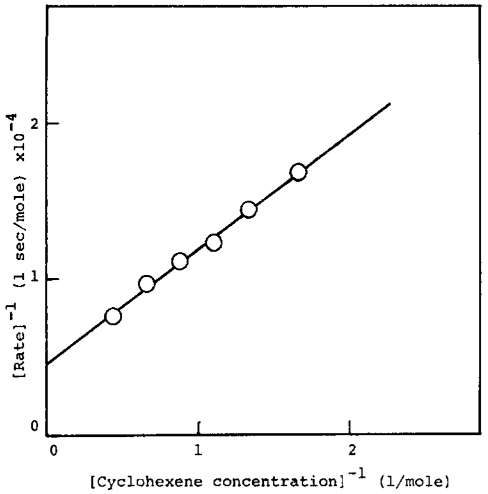


FIG. 10. Plot of the reciprocal of rate of hydrogenation of cyclohexene against the reciprocal of the olefin concentration.

from Fig. 13. The rates are constant in the range of concentration of styrene and 1,3-cyclooctadiene above 0.1 and 0.3 mol liter^{-1}, respectively.

Rates were measured at three temperatures between 0 and 25°C for various concentrations of styrene and 1,3-cyclooctadiene ranging above 0.1 and 0.3 mol liter^{-1}, respectively. The rates retain the corresponding constant at each temperature. The constant values and rate constants derived from them are given in Table 7.

Kinetic Data

From a plot of log k_2 against $1/T$, which is linear, a value for the activation energy E_a was obtained, and the values of kinetic parameters are given in Table 8.

Discussion of Kinetic Results

The polymer-bound palladium complex was divalent before and after use for olefin hydrogenation. When the catalyst was pretreated with hydrogen in the presence of a solvent, the color of the catalyst changed from yellow to green and the induction period in hydrogenation disappeared. Then, a hydride complex seems to be formed by the heterolytic fission of hydrogen by replacing one of the chlorines on the palladium.

$$\text{Ⓟ} -\mathrm{PdCl_2} + \mathrm{H_2} \rightarrow \text{Ⓟ} -\mathrm{PdHCl} + \mathrm{HCl}$$

Homolytic fission of hydrogen is unlikely under the reaction conditions.

The present hydrogenation accompanies the migration of double bonds. 1,5-Cyclooctadiene was isomerized very rapidly to 1,3-cyclooctadiene, which was then hydrogenated so fast that it is not observed in the system. Similarly, terminal olefins are isomerized to internal olefins which are then more slowly hydrogenated. However, the isomerization does not occur in the absence of hydrogen. The stepwise migration of the double bonds was catalyzed by the same palladium–hydride intermediate as hydrogenation. For the nonconjugated dienes and monoenes, it can be said that the rates of Pd–H addition to the double bond and its reverse are much faster than the rate of hydrogenation.

Hydrogenation rates decreased in the order: conjugated dienes > nonconjugated dienes > terminal alkenes > internal alkenes. The order of rates parallels the

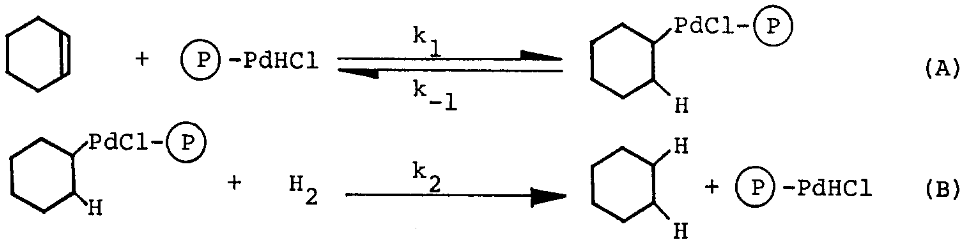
TABLE 6

Data Derived from Plot of Reciprocal of Rate against Reciprocal of Cyclohexene Concentration for Different Values of Reaction Temperature

Temperature (°K)	Gradient [(sec) × 10^{-3}]	Intercept [(sec liter mol^{-1}) × 10^{-3}]	Rate constant k_2 [(liter mol^{-1} sec^{-1})]
273.0	17.8	11.0	6.60
285.5	8.78	7.25	9.38
298.0	7.30	4.50	14.0

relative stabilities of π-bonded Pd–olefin intermediates toward olefin dissociation and also the predicted relative stabilities of the alkyl–palladium intermediates formed from the corresponding olefins toward Pd–H elimination. The stabilities of the alkyl–palladium intermediates would be predicted to decrease in the order: π-allyl complexes (formed from conjugated dienes) > σ, π-chelated complexes (from nonconjugated dienes) > *n*-alkyl complexes (from terminal alkenes) > s-alkyl complexes (from internal alkenes) (*14*).[3] Many π-allyl complexes of palladium (II) have been isolated. But the alkyl complexes are usually unstable (*15*). The hydrogenation of isoprene, 1,3-cyclooctadiene, or styrene is very rapid and a π-allyl intermediate is undoubtedly formed in these hydrogenations.

By considering the characteristics of the reaction mentioned above, we can present a formal scheme containing Pd–H species for the hydrogenation of cyclohexene.



SCHEME II

The double bond adds to the metal hydride to form a σ-alkyl complex, followed by the attack of hydrogen to give cyclohexane and the metal hydride. This mechanism resembles that favored for the $HRuCl(PPh_3)_3$ or $HRu(CO)(PPh_3)_3$ system (*16*).

Using the principles of steady state, the rate *R* is

$$R = -\frac{d[S]}{dt} = \frac{k_1k_2[S][H_2][A]}{k_{-1} + k_1[S] + k_2[H_2]}, \quad (1)$$

where k_1, k_{-1}, and k_2 are the rate constants for the reaction equations (A) and (B) (Scheme II), $[H_2]$ is the concentration of hydrogen in the solution, and $[S]$ and $[A]$ are the substrate and catalyst concentration, respectively. The above rate expression is found to reasonably accommodate most of the experimental data described earlier for the hydrogenation of cyclohexene. As derived from a plot of the reciprocal of rate against the reciprocal of cyclohexene concentration (Fig. 8), the intercept on the *y* axis equals $1/k_2[H_2][A]$, and the rate constant k_2 for the rate-determining step is evaluated from the value of the intercept and is given in Table 6.

If $k_1[S] \gg k_{-1} + k_2[H_2]$, Eq. (1) reduces to the simple form

$$R = -\frac{d[S]}{dt} = k_2[H_2][A]. \quad (2)$$

The rate expression reasonably accommodates the experimental data for styrene and 1,3-cyclooctadiene. The above as-

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[3] The relative hydrogenation rates for a variety of alkenes and alkadienes in the case of $RuCl_2(CO)_2(PPh_3)_2$ are similar to those in the case of the polymer palladium catalyst. The sequence in the rates can be correlated with the relative stabilities of π-bonded Ru–olefin intermediates followed by olefin dissociation and also the predicted relative stabilities of the alkyl–ruthenium intermediates followed by β–H elimination.

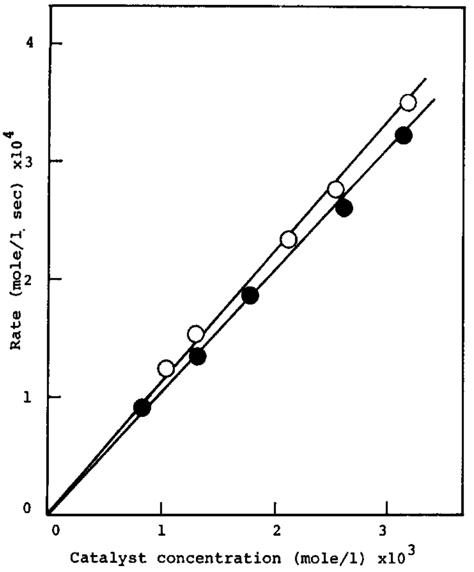

FIG. 11. Dependence of rate of hydrogenation of styrene (○) and of 1,3-cyclooctadiene (●) on catalyst concentration with 0.333 *M* styrene and 0.307 *M* 1,3-cyclooctadiene at 25°C.

sumption is reasonable because styrene and 1,3-cyclooctadiene add to the metal hydride to form a more stable π-benzyl and π-allyl intermediate, respectively. Only conjugated dienes were selectively hydrogenated to the monoene in the presence of both a conjugated diene and a monoene, and the monoene was neither hydrogenated nor isomerized. This fact shows that the conjugated dienes coordinate more strongly to the metal hydride than monoenes. It seems that the fast hydrogenation rate of conjugated dienes may be attributed to the formation of π-allyl intermediates.

The kinetic data at 25°C for hydrogenations of cyclohexene, styrene, and 1,3-cyclooctadiene, obtained from these studies, are given in Table 8. The activation entropies $\Delta S^\ddagger$ are negative. The decrease in entropy corresponds to a considerable loss of freedom due to fixation of the catalyst molecule on the polymer matrix. Furthermore, the values of frequency factor *A* are about 10^4 to 10^7, and are very small compared with those of

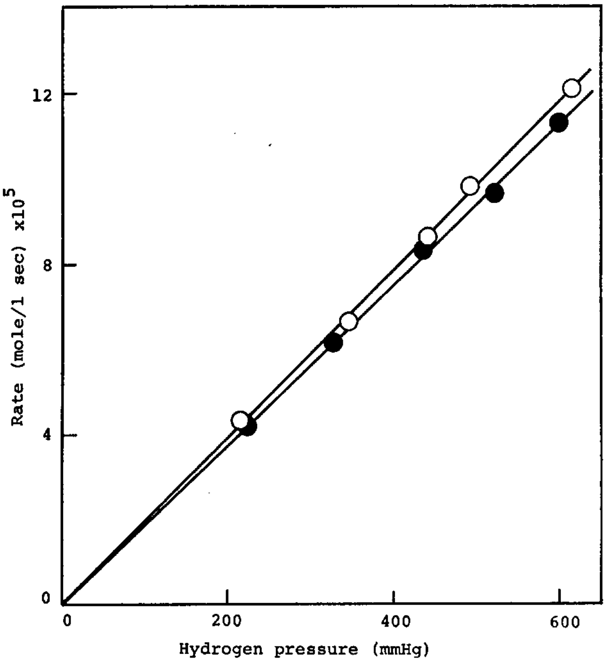

FIG. 12. Dependence of rate of hydrogenation of styrene (○) and of 1,3-cyclooctadiene (●) on hydrogen pressure with 1.32 m*M* catalyst, and 0.333 *M* styrene and 0.920 *M* 1,3-cyclooctadiene at 25°C.

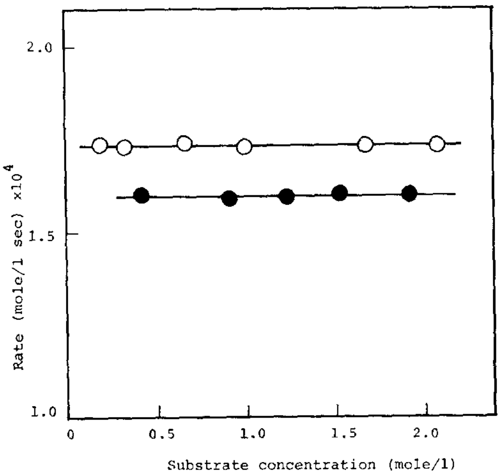

FIG. 13. Dependence of rate of hydrogenation of styrene (○) and 1,3-cyclooctadiene (●) on the substrate concentration with 1.32 mM catalyst at 25°C.

liquid-phase homogeneous reactions, which are ordinarily about 10^{12}. The facts seem to show that the reaction occurred in a liquid–solid heterogeneous system. Activation enthalpies $\Delta H^{\ddagger}$ are much smaller than those expected in homogeneous systems (*17*). It is due to the decrease in enthalpy that the polymer catalyst displays a high activity in spite of the small value of activation entropy. These kinetic data are similar to those which we have already reported for the hydrogenation of styrene with a polymer-bound rhodium (II) chloride complex ($\Delta H^{\ddagger} = 4.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -37.1$ e.u., $A = 1.29 \times 10^5$) (*12*).

The kinetic characteristics of catalysis with this heterogenized complex resemble those of the heterogeneous catalysis rather than the homogeneous catalysis (*18*).

Deuteration and Stereochemistry of Addition of Hydrogen to Olefins

In order to determine the stereochemistry of addition of hydrogen to a double bond, the hydrogenations of dimethyl maleate and dimethyl fumarate were carried out in the presence of deuterium (*19*). From dimethyl maleate, the product was *meso*-dimethyl-2,3-dideutero succinate, and from dimethyl fumarate, the product was DL-dimethyl-2,3-dideutero succinate. These results show that *cis*-deuteration of a double bond occurs exclusively in the presence of the polymer complex.

Comparison with Bailar's Work (*3*)

Bruner and Bailar have prepared a polymer-bound palladium complex by a reaction of dichlorobisbenzonitrilepalladium (II) with phosphinated polystyrene with a 2% cross-linking. The major differences of the reactivity between our complex (C–A) and Bailar's (C–B) are

TABLE 7

Data Derived from Plot of Rate against Substrate Concentration for Different Values of Reaction Temperature

Substrate	Temperature (°K)	Constant value [(mol liter^{-1} sec^{-1}) × 10^5]	Rate constant k_2 [liter mol^{-1} sec^{-1}]
Styrene	273.0	4.10	11.1
Styrene	281.0	6.80	17.9
Styrene	290.0	12.3	30.6
Styrene	298.0	17.4	41.2
1,3-Cyclooctadiene	273.0	4.00	10.8
1,3-Cyclooctadiene	288.0	8.90	22.4
1,3-Cyclooctadiene	298.0	16.0	37.9

TABLE 8

Kinetic Data for the Hydrogenation of Cyclohexene, Styrene, and 1,3-Cyclooctadiene

Substrate	$\Delta H\ddagger$ (kcal mol^{-1})	$\Delta S\ddagger$ (e.u.)	k_2^H/k_2^D	A
Cyclohexene	3.9	−40.3	1.2	2.63×10^4
Styrene	7.9	−24.5	1.5	6.81×10^7
1,3-Cyclooctadiene	7.5	−26.2	1.7	3.11×10^7

shown as follows:

(i) (C–A) was prepared by the method of the bridge-splitting reaction, while (C–B) was prepared by the method of the ligand-exchange reaction.

(ii) (C–A) is much more active. The hydrogenation of styrene was carried out using (C–B) prepared with the same resin (P-1) as used in the preparation of (C–A). (C–A) catalyzed the hydrogenation about 10 times as fast as (C–B).

(iii) When alcohol is used as a solvent, the hydrogenation with (C–B) proceeds under mild conditions, but nonalcoholic solvents require higher pressures for an equally rapid reaction. On the other hand, (C–A) displays high activity in oxygen-containing solvents such as dimethylformamide, ethanol, acetone, and tetrahydrofuran under mild conditions.

(iv) Using (C–B), no isomerizations were observed, while in the case of (C–A), nonconjugated dienes and external olefins were isomerized very rapidly.

Although differences in the electron density on the palladium and chlorine atom were observed, as shown in Table 3, it is not clear why the complexes display different reactivities for hydrogenation.[4]

Comparison with an Analogous Homogeneous Catalyst System, $PdCl_2(PPh_3)_2$–$SnCl_2$

The polymer complex is much more active for hydrogenation of olefins than an analogous homogeneous catalyst. Our studies were run under mild conditions, while the homogeneous catalyst requires a higher pressure of hydrogen and stannous chloride as an activating agent. Stannous chloride is a strong π-acceptor and reduces electron density on the palladium atom, consequently, nucleophiles such as hydride ion or an olefinic double bond can easily coordinate to the metal. On the other hand, the polymer complex catalyst does not need stannous chloride since it has lower electron density on the palladium atom and on the chlorine atom, as shown in Table 3. Therefore, stannous chloride coordinates strongly to the vacant sites only to disturb the coordination of hydrogen or an olefin. It is considered that the higher activity of the polymer complex is due to the difference of electronic and coordinate unsaturation.

The homogeneous catalyst hydrogenates nonconjugated dienes at a faster rate than conjugated dienes (*3*). On the other hand, the polymer catalyst displays its reverse activity. The reactivity of the polymer catalyst was discussed in detail earlier. In the case of the $PdCl_2(PPh_3)_2$–$SnCl_2$ system, the second carbon–carbon double bond occupies the fifth coordination site in the intermediate derived from the addition of the metal hydride to a conjugated diene, while in the case of the polymer catalyst, the coordination number

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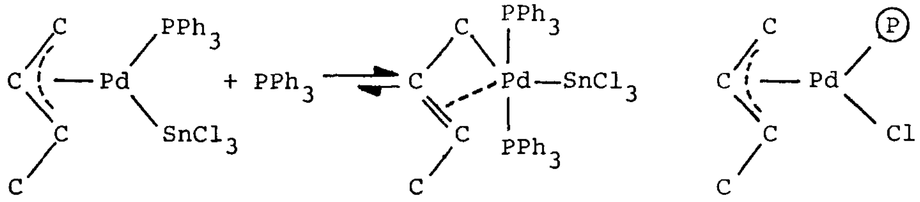
[4] We are grateful to a referee who suggested that differences between (C–A) and (C–B) look like diffusion or ligand equilibria may play a role in (C–B) versus (C–A).

of the π-allyl intermediate is four.



SCHEME III

That is to say, in the homogeneous catalyst system there is no vacant site easily available for the coordination of hydrogen. Therefore, nonconjugated dienes seem to be hydrogenated more rapidly than conjugated dienes, contrary to the polymer system.

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