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Heterogeneous Selective Catalysis of the Hydrogenation of Olefins by Polymeric Palladium(II) and Platinum(II) Complexes

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The preparations of a polymeric diphenylbenzylphosphine ligand and of palladium(II) and platinum(II) dichloride complexes of that ligand are described. The metal complexes are then employed as catalysts for the hydrogenation of olefins. The effect of changing solvent and olefin substrate on catalyst activity and catalyst selectivity for the formation of monoolefins from polyolefins is reported. Activation of the palladium catalyst by alcohol solvents is noted and deuteration studies to determine the source of the hydrogen added to the olefins are described. Mechanisms are proposed for the palladium-catalyzed reductions in alcohols and in the nonprotic solvent systems. The platinum(II) polymeric catalyst is also employed as a catalyst, but more forcing reaction conditions and the presence of tin(II) chloride are required for catalysis to occur.

A great deal of interest has been shown recently in heterogeneous catalysis by polymeric transition metal complexes.[1] Several catalyst systems have been based upon a polymeric ligand formed by placing substituents on a polystyrene base. Haag and Whitehurst[2-5] have substituted cross-linked polystyrene resins with various organic functional groups, such as sulfonates, phosphines, and amines. Group VIII metal complexes of these ligands were then prepared, and these compounds were employed as catalysts for a variety of organic reactions. A polymeric rhodium(I) catalyst for the hydroformylation of olefins was prepared from a polymeric phosphine ligand which was formed by the reaction of sodium diphenylphosphide with a chloromethylpolystyrene.

Grubbs and Kroll[6] have employed a similar catalyst for the hydrogenation of several monoene substrates at room temperature and atmospheric pressure. Their polymer was prepared by the equilibration of $RhCl(PPh_3)_3$ with a phosphine polymer synthesized from the reaction of lithiodiphenylphosphine with chloromethylated polystyrene beads. Such catalysts can be recovered by filtration and reused many times without loss of activity. From the high dependence of the rate of reduction on the size and rigidity of the olefin substrate, the authors proposed that the reductions occur within the pores of the bead.

Collman and coworkers[7] have reported the preparation of a variety of rhodium, iridium, and cobalt complexes with a polymeric triphenylphosphine ligand. They observed a high level of catalytic activity which was attributed to the inability of the resin-bound catalyst to form metal aggregates in solution.

In the study reported here, the platinum and palladium complexes of the polymeric diphenylbenzylphosphine ligand are investigated as selective hydrogenation catalysts for the reduction of polyolefins to monoolefins. Some information regarding both metal-containing polymeric catalysts has already been reported.[8] When the olefin substrate is dissolved in alcohol, the catalytic activity of the palladium-containing polymer is sufficient to permit the hydrogenation to proceed at room temperature under a hydrogen atmosphere within 3-6 hr. Other solvents require higher pressures for an equally rapid reaction. Not surprisingly, the catalytic activity of the metal-containing polymers was shown to decrease as the quantity of metal in the polymer decreases. With most of the metal-polymer preparations, significant hydrogenation will, however, occur at room temperature. The platinum polymer system requires the addition of tin(II) chloride and reaction conditions of 150° and 550 psi of hydrogen. Last, the heterogeneity of the catalytic process with both metal complexes was shown by the recovery of the catalysts by filtration and reuse several times with only a small loss in catalytic activity after the first use and no further loss thereafter.

Experimental Section

Materials. Analytical grade chemicals and solvents were employed and were, in most cases, used without further purification. Whenever dry, air-free solvents were needed, the commercial solvents were refluxed over calcium hydride for a minimum of 24 hr under a nitrogen atmosphere before distillation. The purity of the olefins and solvents used in the hydrogenation experiments was always checked by gas chromatographic analysis to determine the initial percentage of possible isomerization and hydrogenation products.

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Table I. Microanalytical Data of the Polymeric Diphenylbenzylphosphine Ligands

	Percentage				
	C	H	P	Cl	Empirical formula[a]
1st phosphine prepn, P1	75.55	6.39	7.19	4.60	$C_{48}H_{49}ClO_3P_2$
2nd phosphine prepn, P2	77.16	6.34	5.82	5.54	$C_{68.3}H_{68.3}Cl_{1.7}O_{3.3}P_2$
3rd phosphine prepn, P3	78.64	6.41	6.02	3.88	$C_{67.5}H_{66.1}Cl_{1.1}O_{3.3}P_2$

[a] Oxygen content calculated by difference.

Soybean methyl ester was prepared as described by Hartman[9] from refined soybean oil provided by Dr. E. N. Frankel of the Northern Regional Research Laboratory of the U. S. Department of Agriculture.

Dichlorodibenzonitrilepalladium(II) and dichlorodibenzonitrileplatinum(II) were prepared by the method of Kharasch, Seyler, and Mayo.[10]

Chloromethylated Amberlite XAD-4 was a gift of the Rohm and Haas Company. It was obtained as hard, insoluble 20–50 mesh spheres of approximately 1-cm^3/g porosity. The polymer was received still wet. It was dried in a rotary evaporator at 50° for 12 hr before being used. The compound analyzed as 72.59% carbon, 6.43% hydrogen, and 19.16% chloride for an empirical formula of $C_{11}H_{12}Cl$.

An organic polymer containing benzyldiphenylphosphine functional groups was prepared by the method of Haag and Whitehurst.[5] Table I presents the analytical data for three preparations of the polymeric diphenylbenzylphosphines. As oxygen analysis could not be obtained in the presence of phosphorus, all of the compound not accounted for by carbon, hydrogen, chloride, or phosphorus analyses was assumed to be oxygen in the calculation of the empirical formulas. For the first two phosphine–polymer preparations, the chloromethylated Amberlite was used in its original form. Before the third preparation, the starting material was ground for 8 hr in a ball mill to a fine powder. No appreciable improvement in phosphorus uptake was observed.

Metal-Phosphine Complexes. All of the polymeric metal-phosphine complexes were prepared in approximately the same manner. The synthesis of $P3\cdot(PdCl_2)_{0.999}$ is typical. Under a nitrogen atmosphere, 2.07 g of P3 was suspended for 60 hr in 1000 ml of a refluxing acetone solution containing 0.844 g of dichlorodibenzonitrilepalladium(II). After cooling, the yellow product was recovered by filtration. The solid was slurried three times in 500 ml of acetone and then washed with one 500-ml portion of ether. The product was dried for 24 hr under vacuum. None of the benzonitrile starting material could be observed in the Nujol mull infrared spectrum of the product. In preparations involving the other phosphines, the ligands were ground to a fine powder in a ball mill or mortar before the coordination of the metals. The analytical data for the various preparations of the metal complexes are summarized in Table II. The empirical formulas are calculated from the carbon analyses assuming no change in the composition of the ligand during the complexation reaction. The chloride analyses calculated from the empirical formulas correlate well with the observed values. In the one case in which the palladium analysis was obtained, the result agrees with the calculated value.

Instruments and Hydrogenation Procedure. In the high-pressure hydrogenations, the reactants were mixed in a glass vessel, which was then placed in a 300-ml stainless steel Magne-Drive autoclave equipped with an air-driven stirrer and a valve to permit sampling without interruption of the reaction. With reactions carried out at room temperature, the autoclave was flushed three times with hydrogen before being pressurized to the desired level and the stirring was begun. When elevated temperatures were needed, the autoclave was partially pressurized and then heated, with stirring, to the desired temperature. If necessary, the pressure was then adjusted.

For the atmospheric pressure hydrogenations, the catalyst and additive (if any) were placed in the reaction flask and the vessel was flushed with hydrogen for a minimum of 5 min. With a positive hydrogen flow continuing, the desired quantities of solvent and olefin substrate were quickly added. The reaction flask was then sealed and stirring was begun. Sampling was done *via* syringe.

The reactions were not considered to have begun until the system was at the desired temperature and pressure and the stirring had been started. All reaction times reported were measured from this point. Although "initial" samples were usually taken at this time, little or no hydrogenation or isomerization had occurred in any of the reactions studied.

Table II. Analytical Data of the Polymeric Diphenylbenzylphosphine–Metal Complexes

Obsd anal., %				
C	H	Cl	Empirical formula calcd from C	Theoret % Cl calcd from empirical formula
62.51	5.28	10.77	$P1\cdot(PdCl_2)_{0.851}$	10.41
65.71	5.16	8.88	$P1\cdot(PdCl_2)_{0.600}$	8.91
66.89	5.19	8.61	$P1\cdot(PdCl_2)_{0.524}$	8.41
66.94	5.48	8.18	$P1\cdot(PdCl_2)_{0.507}$	8.30
68.36	5.33	7.80	$P1\cdot(PdCl_2)_{0.406}$	7.63
67.77	5.38	9.82	$P2\cdot(PdCl_2)_{0.824}$	9.82
67.10	5.31	8.95	$P3\cdot(PdCl_2)_{0.999}$	9.11[a]
63.66	5.13	8.34	$P1\cdot(PtCl_2)_{0.505}$	8.30

[a] Pd analysis was obtained on this complex: obsd, 8.86%; calcd from empirical formula, 8.84%.

In the one atmospheric pressure hydrogenation study in which the measurement of hydrogen uptake was desired, the reaction was run in a 10-ml erlenmeyer flask with a stopcock side arm connected to a mercury manometer system.

Infrared absorption spectra were recorded on a Perkin-Elmer 457-5001 spectrophotometer. A MAT CH-7 mass spectrometer and a Varian Aerograph 1700 gas chromatograph were employed in the 6C mass spectrometer studies.

All other gas-phase chromatographic analyses were performed on a Varian Aerograph 6C 1520 gas chromatograph using flame ionization detection. All hydrogenations and isomerization products were identified by their retention times on gas chromatographic columns by comparison with retention times of authentic samples of known composition.

Results and Discussion

Infrared Studies. Due to the complete insolubility of the polymeric complexes in all solvents (except powerful oxidizing acids), structural studies were necessarily limited to mull spectra.

The mull infrared spectra of the metal-phosphine polymers each contain one band not found in the spectra of the phosphine ligand. These bands occur at 351 and 339 cm^{-1} for the palladium and platinum complexes, respectively. The $PdCl_2[PPh_2(CH_2Ph)]_2$ and $PtCl_2[PPh_2(CH_2Ph)]_2$ complexes were also synthesized[11-13] and showed bands in this area at 352, 306, 284 and 336, 308, 285 cm^{-1}, respectively.

A recent study summarized the positions of absorption bands identified as metal-halogen stretching frequencies in the infrared spectra of several compounds of the general form MCl_2P_2 (where M = Pd or Pt and P is a tertiary phosphine or arsine).[14] The trans metal-chloride stretch is between 350 and 360 cm^{-1} for palladium complexes and between 326 and 340 cm^{-1} for the platinum compounds. With the cis isomers, two infrared-active bands appear at

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310-314 and 286-304 cm^{-1} in palladium compounds and 302-312 and 277-293 cm^{-1} in platinum systems.

The results would seem to indicate that the monomeric $Pd[PPh_2(CH_2Ph)]_2Cl_2$ and $Pt[PPh_2(CH_2Ph)]_2Cl_2$ complexes exist, as expected, as a mixture of cis and trans isomers. The polymers appear to exist exclusively in the trans configuration. A study of molecular models of the smallest single unit of the polymer supports this conclusion. The model of the cis form of the complex, unlike that of the trans form, could not be prepared without considerable overlap of the π clouds of the benzene rings from the benzyl group on the phosphine.

Palladium-Phosphine Polymer System. The palladium-containing polymeric catalyst displayed good selectivity for the formation of monoolefins under the proper reaction conditions at both high and low pressures. Figures 1 and 2 show the results of the hydrogenation of soybean methyl ester with the catalyst suspended in methylene chloride at 550 psi of hydrogen and 25° and 50% methanol-50% benzene at 25° under a hydrogen atmosphere at atmospheric pressure.

High-Pressure Reactions. Although all nonalcoholic solvents necessitated the use of higher pressures of hydrogen for a conveniently rapid reaction, the rate of the hydrogenation at the higher pressure was greatly affected by changes in these solvents.

Table III summarizes the results of the reduction of soybean methyl ester in a variety of solvents with either $P1 \cdot (PdCl_2)_{0.507}$ or $P1 \cdot (PdCl_2)_{0.851}$ as the catalyst. Among the solvents tested for the selective hydrogenation of olefins, methylene chloride was found to be the best. In carbon tetrachloride and, to a lesser extent, in chloroform, the polymeric metal complex tended to coagulate and to float on the surface of the solvent, resulting in very little contact with the olefin and little hydrogenation. In methanol, a large increase in catalyst activity and complete loss of selectivity were observed. This will be discussed in more detail later in regard to atmospheric pressure hydrogenations. In alkane solvents, the catalyst activity is approximately the same as in methylene chloride, but, unfortunately, the reduction of the monoene fractions also occurs readily. When the reaction was run in acetone or benzene, the rate of reduction was decreased considerably, and again, little selectivity was displayed. Acetone, with its unshared pairs of electrons on the oxygen, and benzene, with its π electrons, are capable of coordination to palladium and may hinder the attachment of hydrogen and olefin to the metal and decrease the rate of hydrogenation. In the same way, triphenylphosphine and thiophene, both good coordinating agents, poison catalytic activity when added in trace quantities to the hydrogenation mixture in methylene chloride. The addition of the poor coordinating agent, triphenylphosphine oxide, to the substrate in methylene chloride has no effect on the reaction.

Table IV shows the results of hydrogenation of the several hexadiene isomers. The conjugated isomers were reduced more rapidly and with greater selectivity than the nonconjugated. No isomerization was observed between the diene isomers. By studying the isomeric distribution of product hexenes, it can be determined whether the addition of hydrogen is 1,2 or 1,4 addition. Unfortunately, the interpretation of the monoene isomer distribution is complicated by the inability of the silver nitrate-ethylene glycol chromatographic column used in this study sufficiently to resolve 1-hexene and the cis 2- and 3-hexenes. The product distribution is, however, not inconsistent with 1,2 addition being the predominant mode of reaction.

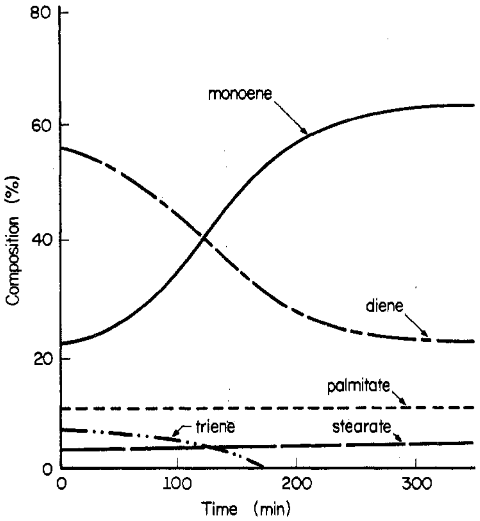

Figure 1. Hydrogenation of soybean oil methyl ester in methylene chloride catalyzed by $P1 \cdot (PdCl_2)_{0.851}$ at 550 psi of hydrogen and room temperature.

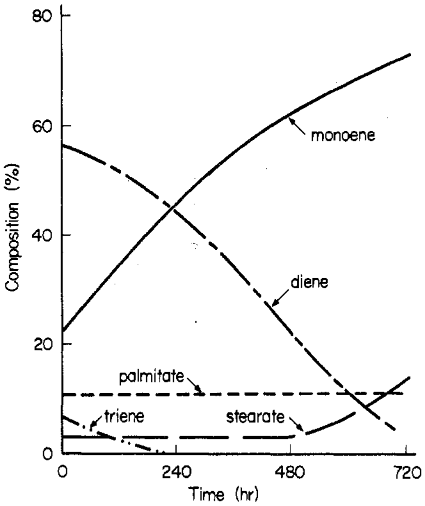

Figure 2. Hydrogenation of soybean oil methyl ester in 50% methanol-50% benzene catalyzed by $P3 \cdot (PdCl_2)_{0.999}$ at room temperature and 1 atm of hydrogen.

Individual fatty acid derivatives were also hydrogenated. A very high level of selectivity is shown by the failure of methyl elaidate to be reduced after 3 hr at 550 psi of hydrogen and 70° with the $P1 \cdot (PdCl_2)_{0.507}$ catalyst. Conjugated methyl *trans,trans*-linoleate was completely reduced to monoene after 3 hr under the same conditions, a significantly faster reaction than the reduction of the nonconjugated polyolefins.

Atmospheric Pressure Hydrogenations. If the same catalyst-to-olefin ratio is used in the atmospheric pressure reductions as in the pressurized hydrogenations (40 mg of catalyst/1 ml of olefin), the reactions proceed far too fast to be studied easily. After 90 min at room temperature and 1 atm pressure of hydrogen with $P1 \cdot (PdCl_2)_{0.600}$ catalyst in methanol solvent, a sample of 2,4-hexadiene was reduced, 86.2% to hexenes and 3.5% to hexane. Halving the catalyst-to-olefin ratio greatly reduced the rate of the reduction, leaving 20% of the hexadiene unreduced after 2 hr under the same conditions. Since this slower rate was much more convenient for our gas chromatographic analyses, this lower

Table III. Catalytic Hydrogenation of 2 ml of Soybean Methyl Ester in 70 ml of Solvent Using 85 mg of P1 · $(PdCl_2)_n$ Catalyst under 550 Psi of Hydrogen for 3 Hr

			% compn of product[a]			
Solvent	*n*	Temp, °C	Triene	Diene	Monoene	Saturate
Methylene chloride	0.507	70		17.7	68.9	13.6
Methylene chloride	0.851	25	1.1	30.3	53.4	15.1
Chloroform	0.507	70	4.5	47.9	30.8	16.8
Carbon tetrachloride	0.507	70	6.8	55.4	23.3	14.0
Acetone	0.507	70	4.4	38.0	36.9	20.7
Hexane	0.507	70		6.2	60.4	33.2
Methanol	0.507	70			7.0	92.9
Benzene	0.851	25	5.3	45.4	30.6	18.3
Pentane	0.851	25	1.9	38.1	40.0	20.0

[a] The initial composition was 14.2% saturate, 22.3% monoene, 56.2% diene, and 7.0% triene.

Table IV. Hydrogenation of Hexadiene Isomers Using 40 mg of P3 · $(PdCl_2)_{0.999}$ Catalyst in Methylene Chloride Solvent at 550 Psi of Hydrogen and 25° for 3 Hr

	% compn of product				
		Hexene isomers			
Initial olefin	Hexadiene	Trans 2	Trans 3	Other	Hexane
2,4-Hexadiene		65.1	12.4	19.3	3.2
1,3-Hexadiene	40.6	17.3	20.4	21.6	Trace
1,5-Hexadiene	63.4	9.0	Trace	25.2	2.4

ratio of catalyst to olefin was used in the reactions at this pressure.

Table V summarizes the results of a series of hydrogenations of 2,4-hexadiene in a variety of alcoholic solvents and solvent mixtures. The activity of the catalyst decreases with increasing length and branching of the alkyl chain of the alcohol. This could result from the decreasing acidity of the alcohol proton or the increasing steric size of the alkyl group. Since activation of the catalyst presumably results from preliminary coordination of the alcohol to the metal before attack of olefin, the steric effect seems the more important. In the case of ethylene glycol, the second alcohol group may be acting as a poison, just as other coordinating agents do.

An increase in the concentration of the thermodynamically unfavored cis,trans isomer occurred in 1-butanol and the mixed-solvent systems. No formation of *cis,cis*-2,4-hexadiene or any of the other hexadienes was observed in any of the solvent systems studied. If trace quantities of triphenylphosphine or thiophene were added in the catalytic hydrogenation of 2,4-hexadiene in methanol to stop the reduction, up to 90% of the 2,4-hexadiene was isomerized to the cis,trans form.

A more limited investigation of the effect of changes in solvent on the reduction of soybean methyl ester is displayed in Table VI. The hydrogenations were not as selective as might have been expected from the results with hexadiene. Highest selectivity was obtained in 50% benzene-50% methanol solution, but, as Figure 2 shows, this selectivity was shown only when sufficient unreacted diene was present. Unlike the results with the $Pd(PPh_3)_2Cl_2$ catalyst,[12] no transesterification was observed in the hydrogenation in butanol.

The hydrogenations in 50% methanol-50% benzene were run on the positional isomers of hexadiene, cyclohexadiene, and hexene using the P3 · $(PdCl_2)_{0.999}$ catalyst at room temperature and 1 atm of hydrogen. The results are summarized in Tables VII-IX. No isomerization was observed between positional isomers of the dienes, and the conjugated isomers were reduced more rapidly than nonconjugated. As in the pressurized hydrogenations, the products of the reductions of the hexadienes appear to be the result of 1,2 addition of hydrogen. In the absence of dienes, the monoenes were extensively isomerized and reduced. The order of hydrogenation of various hexene isomers (1- > *cis*-2- > *trans*-2- > *cis*-3- > *trans*-3-hexene) suggests a simple steric effect on coordination to the catalyst. The failure to observe any reduction of methyl elaidate in the pressurized hydrogenations may be an extreme example of this steric effect.

To investigate the possibility that the hydrogen source for the reduction in the alcoholic solvents was the alcohol proton, a hydrogenation was attempted under an argon atmosphere. When 1 ml of 2,4-hexadiene and 20 mg of P1 · $(PdCl_2)_{0.600}$ were stirred in methanol under argon at room temperature, no reduction or isomerization occurred after 15 hr. Ninety minutes after the reaction flask was flushed with hydrogen, the olefin substrate consisted of 15.3% 2,4-hexadiene, 81.2% hexenes, and 3.5% hexanes.

Table V. Hydrogenation of 1 ml of 2,4-Hexadiene in Various Solvents Using 20 mg of P3 · $(PdCl_2)_{0.999}$ Catalyst at Room Temperature and Atmospheric Pressure of Hydrogen

		% compn of product[a]			
Solvent	Time, hr	*cis,trans*-2,4-Hexadiene	*trans,trans*-2,4-Hexadiene	Hexene	Hexane
Methanol	3			78.8	21.2
Ethanol	3			95.5	4.5
1-Butanol	3	37.6	14.1	47.6	0.7
1-Butanol	6			91.7	8.3
2-Propanol	3	7.6	50.3	41.5	0.6
2-Propanol	5		16.5	82.6	1.0
tert-Butyl alcohol	3	12.5	60.1	26.5	0.8
tert-Butyl alcohol	5	5.1	42.1	51.4	2.2
Ethylene glycol	4	30.8	58.5	10.8	
Ethylene glycol	8	10.7	57.1	32.1	
Methanol-benzene[b]	4	33.8	17.6	48.6	
Methanol-methylene chloride[b]	4	68.3	13.2	18.5	

[a] The initial composition was 67.4% *trans,trans*- and 32.6% *cis,trans*-2,4-hexadiene. [b] Equal volumes of each solvent were used.

Table VI. Hydrogenation of 1 ml of Soybean Methyl Ester in Various Solvents Using 20 mg of P3·$(PdCl_2)_{0.999}$ Catalyst at Room Temperature and Atmospheric Pressure of Hydrogen

Solvent	Time, hr	% compn of product[a] Diene	Monoene	Saturate
Methanol	3	2.5	72.5	24.9
75% methanol–25% benzene	8	4.0	73.0	22.5
50% methanol–50% benzene	8	23.4	62.4	14.3
1-Butanol	8	13.9	67.7	18.3

[a] The initial composition was 14.2% saturate, 22.3% monoene, 56.2% diene, and 7.0% triene. There was no triene in the product.

Table VII. Hydrogenation of the Hexadiene Isomers Using 20 mg of P3·$(PdCl_2)_{0.999}$ Catalyst in 50% Methanol–50% Benzene Solvent at Room Temperature and Atmospheric Pressure for 4 Hr

	% compn of product				
		Hexene isomers			
Initial olefin	Hexadiene	Trans 2	Trans 3	Other	Hexane
2,4-Hexadiene	51.4[a]	22.0	12.0	14.7	
1,3-Hexadiene	43.7	12.8	21.0	22.5	
1,4-Hexadiene	64.2	22.6		13.2	Trace
1,5-Hexadiene	85.7	4.5		9.8	Trace

[a] 17.6% *trans,trans*- and 33.8% *cis,trans*-2,4-hexadiene.

Table VIII. Hydrogenation of 1 ml of the Hexene Isomers in 50% Methanol–50% Benzene Solvent with P3·$(PdCl_2)_{0.999}$ Catalyst for 3 Hr at Room Temperature and 1 Atm of Hydrogen

	% compn of product[a]				
		Hexene isomers			
Olefin	Hexane	Trans 2	Cis 2	Trans 3	Cis 3
1-Hexene	35.5	49.7	14.9	Trace	Trace
trans-2-Hexene	15.7	72.2	12.2	Trace	Trace
cis-2-Hexene	24.6	52.4	16.2	4.2	1.6
trans-3-Hexene	10.8	25.0	7.6	53.5	2.6
cis-3-Hexene	16.8	36.0	8.7	30.4	8.1

[a] No 1-hexene in the product.

Deuterium-Labeling Studies. The hydrogenation of 1 ml of 2,4-hexadiene was run at 25° and atmospheric pressure of hydrogen in 75% methanol–25% benzene solution with 20 mg of P3·$(PdCl_2)_{0.999}$ catalyst. The reaction was then repeated twice, once with CH_3OD instead of CH_3OH and once with deuterium in place of hydrogen. After 3 hr, all samples of 2,4-hexadiene were reduced to mixtures of approximately 70% hexenes, 1% hexane, and 29% equal amounts of *cis,trans*- and *trans,trans*-2,4-hexadiene.

Extensive exchange of the methanol proton (or deuteron) was observed in these reactions. The reaction of 2,4-hexadiene in methanol under deuterium resulted in the conversion of approximately 20% of the 15 ml of alcohol solvent to methanol-*d*. When the situation was reversed and methanol-*d* was used in the solvent for a reduction under hydrogen, only 35% of the methanol remained deuterated after 3 hr. Considering the large excess of methanol in the reaction flask, the exchange reaction occurred much more readily than either the isomerization or reduction of the olefin.

Deuterium uptake occurred when either CH_3OD or D_2 was present but was more extensive under the D_2 atmosphere. In methanol-*d* the unreduced 2,4-hexadiene has a peak at $m + 1$ of 10.0% of the molecular ion for the trans,trans and 5.8% of the molecular ion for the cis,trans isomer. Under deuterium, the peaks at $m + 1$ rose to 23.2 and 12.3% of the molecular ion for the trans,trans and cis,trans isomers, respectively. Similarly, the peak at $m + 1$ for the hexene products reduced in methanol-*d* was 28% of the molecular ion, while for the same reaction under D_2, peaks were observed in the mass spectrum up to m/e 89 ($m + 5$). The peak at $m + 1$ was 138%, $m + 2$ was 62%, $m + 3$ was 20%, $m + 4$ was 9%, and $m + 5$ was 7% as intense as that of the molecular ion. Since the uptake of deuterium is greatest when the deuterium is present as a gas, the atmosphere must be the primary source of hydrogen for the reductions in alcohol just as it is for the reductions in other solvents. The presence of deuterated hexene in the reaction run in methanol-*d* and of undeuterated monoene from the reaction run under deuterium gas indicates either that some alcoholic protons are added directly to olefin or that the gaseous products of the exchange reaction between the alcohol proton and the atmosphere react subsequently in the hydrogenation reaction. The more extensive deuterium uptake under deuterium gas indicates that the latter explanation is correct.

Yellow-to-Green Isomerization. An irreversible yellow-to-green change was observed in the catalyst during each hydrogenation reaction at both low and high pressures. The change also occurred in the absence of olefin, and without any uptake of hydrogen.

The stirring of a methanol suspension of the catalyst with 1-hexene for 24 hr under nitrogen failed to cause any color change, but the color change could be effected within 5 min by bubbling ethylene or carbon monoxide into a suspension of the catalyst in methanol. The green form has the same carbon, hydrogen, chloride, and palladium analyses as the yellow and the same infrared spectrum. No explanation can, as yet, be advanced for this phenomenon.

Test of Pd(II) Catalysis. To examine the possibility that the catalytic agent in these hydrogenations was not the Pd(II) complex, but palladium metal, a sample of once-used green P3·$(PdCl_2)_{0.999}$ was suspended in ethanol for 12 hr with a large excess of potassium cyanide to remove any Pd(II) ions from the polymer. Any Pd(0) present would remain, and if it were the only catalytic agent, the polymer would retain its catalytic activity. During the exchange process, the suspended solid changed from green to the white color of the free ligand. The reaction mixture was filtered and washed liberally with hot water, ethanol, acetone, and ether. Only organic cyanide (formed, presumably, by the reaction of $-CH_2Cl$ from polymer with cyanide) could be observed in the Nujol mull spectrum of the recovered polymer.

Table IX. Hydrogenation of the Cyclohexyl Olefins Using 20 mg of P3·$(PdCl_2)_{0.999}$ Catalyst in 50% Ethanol Solutions at Room Temperature and Atmospheric Pressure

			% compn of product		
Initial olefin	Solvent	Time, hr	Unreacted diene	Cyclohexene	Cyclohexane
1,3-Cyclohexadiene	Ethanol–benzene	3		98.6	1.4
1,4-Cyclohexadiene[a]	Ethanol–benzene	4	85.0[b]	15.0	Trace
1,4-Cyclohexadiene[a]	Ethanol–methylene chloride	4	71.7	26.7	1.6
Cyclohexene	Ethanol–benzene	4		89.9	10.1

[a] The initial composition was 98.3% 1,4-cyclohexadiene and 1.7% cyclohexene. [b] Trace of 1,3-cyclohexadiene was present.

After the extraction, the polymer still contained 11% of the original quantity of palladium. While some of this palladium may be in the metallic form, much of it was probably not since the yellow P3·$(PdCl_2)_{0.999}$ (which had never been in contact with hydrogen) gave no increased removal of palladium when treated with cyanide under the same conditions. An attempt to hydrogenate 2,4-hexadiene in methanol with this low-palladium catalyst resulted in no reduction after 3 hr under conditions which had resulted in complete reduction of diene when untreated catalyst was employed.

Mechanism for the Catalytic Process. Although the mechanism of the catalysis is presumed to be similar to that proposed earlier for catalysis by soluble transition metal complexes,[15] the data are insufficient at this time to justify the proposal of a detailed mechanism for the hydrogenation process. Alcohols must activate by reversible coordination to the metal, and the failure to take up very much deuterium in the reactions in CH_3OD means that the alcohol proton must not be directly bound to the metal. Major differences have been noted between the catalytic properties of the palladium-containing polymers and those of their supposed monomeric analog, $PdCl_2(PPh_3)_2$. The polymers are much more active as catalysts. Our studies were run under milder conditions with a catalyst:olefin ratio about 1% as large as that employed in the earlier work with homogeneous catalysts. The stannous chloride activating agent in the earlier work proved to be a poison for these reactions. The activation of the polymeric catalysts by the presence of alcohols was not observed with the monomers. Last, the monomeric catalysts reduced nonconjugated dienes at a greater rate than conjugated ones, the direct opposite of what was observed here. The mechanism for heterogeneous catalysis must, therefore, differ somewhat from that proposed previously for $PdCl_2(PPh_3)_2$ catalysis.

Platinum-Containing Polymer. The results obtained with smaller olefins were similar to those reported earlier for hydrogenation of soybean methyl ester with the platinum-phosphine polymer. After 3 hr at 150° in methylene chloride with P1·$(PtCl_2)_{0.505}$ and $SnCl_2 \cdot 2H_2O$ (Sn:Pt = 10), 2,4-hexadiene was reduced to a product composed of 2% hexane, 19% hexenes, and the rest, 2,4-hexadiene. The reduction of 1,5-hexadiene (shown in Figure 3) under the same conditions occurred with isomerization to all possible position isomers of hexadiene. It would appear that nonconjugated dienes isomerize to conjugated ones and these latter are reduced.

After a hydrogenation, the recovered catalyst was 52.68% carbon, 4.15% hydrogen, and 9.79% chloride. The carbon analysis indicates an empirical formula of $[P1 \cdot (PtCl_2)_{0.505}][SnCl_2]_{1.23}$. The chloride analysis, however, was far short

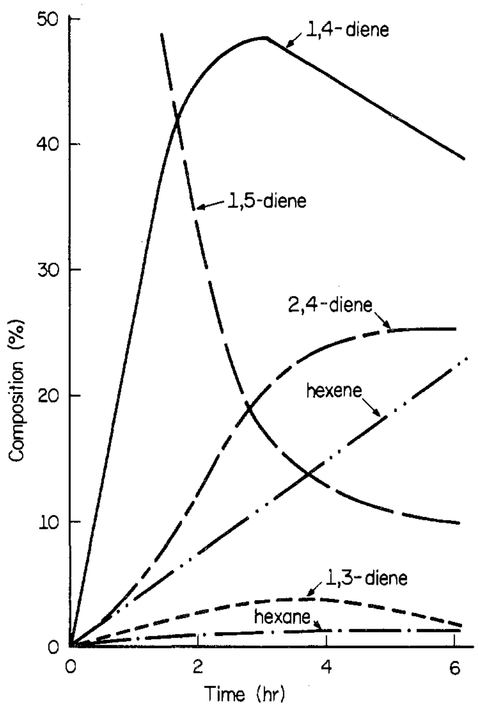

Figure 3. Hydrogenation and isomerization of 1,5-hexadiene in methylene chloride catalyzed by P1·$(PtCl_2)_{0.505}$ + $SnCl_2 \cdot 2H_2O$ at 150° and 550 psi of hydrogen.

of that predicted from this formula and therefore, a simple $SnCl_3^-$ adduct (as is formed in monomeric complexes) is not formed. The $SnCl_3^-$ ligand is a strong trans director and could cause elimination of the trans chloride, but even this would not completely explain the lack of chloride in the final product.

Registry No. Dichlorodibenzonitrilepalladium(II), 14220-64-5; dichlorodibenzonitrileplatinum(II), 14873-63-3; 2,4-hexadiene, 592-46-1; 1,3-hexadiene, 592-48-3; 1,4-hexadiene, 592-45-0; 1,5-hexadiene, 592-42-7; 1-hexene, 592-41-6; *trans*-2-hexene, 4050-45-7; *cis*-2-hexene, 7688-21-3; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cyclohexene, 110-83-8; methylene chloride, 75-09-2; chloroform, 67-66-3; carbon tetrachloride, 56-23-5; acetone, 67-64-1; hexane, 110-54-3; methanol, 67-56-1; benzene, 71-43-2; pentane, 109-66-0; ethanol, 64-17-5; 1-butanol, 71-36-3; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; ethylene glycol, 107-21-1; stannous chloride, 7772-99-8.

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(15) J. Halpern, *Chem. Eng. News*, **44**, 68 (Oct 31, 1966).