

The Selective Hydrogenation of 1,5-Cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and the Formation of an π -Allylic Reaction Intermediate

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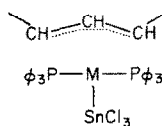
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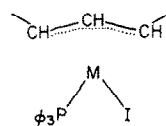
The catalytic selective hydrogenation of 1,5-cyclooctadiene to cyclooctene with soluble $[\text{PdCl}_2(\text{P}\phi_3)_2]$ was studied in detail. The catalyst did not require the addition of SnCl_2 and the reactivity was similar to that of the corresponding heterogeneous Pd(II) polymer catalyst. The isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene preceded the reduction to cyclooctene at 90°C, but the isomerization was slower than the hydrogenation at room temperature. The π -allylic reaction intermediate, $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$, was isolated from the hydrogenation solution and was a much more active catalyst than $[\text{PdCl}_2(\text{P}\phi_3)_2]$; it was quite active even at room temperature. Although an excess of chloride ion did not affect the reactivities of $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$, an excess of triphenylphosphine poisoned them to a remarkable degree. No hydrogenation occurred under a nitrogen atmosphere, but it took place under hydrogen chloride gas to as high a degree as under hydrogen. When both hydrogen and hydrogen chloride are present, the hydrogenation is faster than when under pure hydrogen.

Several soluble Pt(II), Pd(II), and Ni(II) catalysts containing phosphine ligands have been developed for the selective hydrogenation of polyene to monoene (1-14). The characteristics of these homogeneous catalysts are as follows: they bring about the hydrogenation of all but one double bond; they cause the double bonds to move along the hydrocarbon chain until the double bonds become conjugated, the isomerization usually preceding the hydrogenation. Here, the term "selectivity" means that the hydrogenation of the last double bond is extremely slow compared with that of the others. In spite of many studies, however, the reaction mechanism

is still not clear. For example, in the case of $[\text{PtCl}_2(\text{P}\phi_3)_2]$, SnCl_2 is needed as a co-catalyst and the important reaction intermediates have been thought to have the structure I (14). In the case of $[\text{NiI}_2(\text{P}\phi_3)_2]$, the addition of SnCl_2 is not necessary and structure II has been proposed as an important reaction intermediate (14). But such intermediates have not yet been isolated.



Structure I



Structure II

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On the other hand, heterogeneous Pt(II) and Pd(II) polymer catalysts have been

developed recently (15, 16). The Pd(II) catalyst has been found to be more active than the corresponding homogeneous catalyst.

However, there exist some differences between the homo- and heterogeneous Pd(II) catalysts. For example, the addition of SnCl_2 gives a good result in the homogeneous system (5, 14), but it is deleterious in the heterogeneous system (16). Migration of double bonds is much faster than the hydrogenation in the homogeneous system (5, 14), but is slower than the hydrogenation in the heterogeneous system (16). It seems easy to ascribe these differences to a polymer effect; however, detailed study of the homogeneous Pd(II) catalyst is still necessary; there have been few studies of it (5, 14).

In this study, we investigated in detail the selective hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and succeeded in the isolation of the reaction intermediate which corresponds to the type of structure II. The compound is much more active than $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and the reactivity is essentially the same as that of the heterogeneous Pd(II) catalyst.

EXPERIMENTAL

1. *Apparatus.* Infrared absorption spectra were measured in KBr disks using a Perkin-Elmer 467 Grating infrared spectrophotometer. Proton magnetic resonance spectra were run on a Varian EM-390 instrument at 32°C in CDCl_3 solution with TMS as an internal reference. A bench-size 300 ml stainless steel Magne-Drive autoclave was used for pressures higher than 1 atm. Reactions at a pressure of 1 atm were carried out in an Erlenmeyer flask. The hydrocarbon reaction products were analyzed by a Varian Aerograph GC-1520B gas chromatograph employing a thermal conductivity detector. A 10 ft \times 0.25 in. copper column with 20% diethyleneglycol adipate on 60-80 Chromosorb Z was used, and the carrier gas was helium. Column

temperature was 125°C and the carrier gas flow rate was 40 ml/min. Elemental microanalyses and molecular weight measurements were carried out by the University of Illinois microanalytical laboratory.

2. *Reagents and preparation of chemicals.* Analytical grade chemicals and solvents were employed and were, in most cases, used without further purification. $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$ were prepared by methods in the literature (5, 17). We found that under hydrogen pressure the complex $[\text{PdCl}_2(\text{P}\phi_3)_2]$ becomes soluble in various organic solvents. $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ was prepared by hydrogenating a mixture of 2 g (1.4×10^{-3} mole) of $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and 5 g (4.6×10^{-2} mole) of 1,3-cyclooctadiene in CH_2Cl_2 (70 ml) + CH_3OH (30 ml) at 90°C, under 34 atm of hydrogen for about 1 hr. The pale yellow solution was concentrated almost to dryness at room temperature. The precipitate was washed with 150 ml of petroleum ether (bp 30-60°C) and then was dissolved in 250 ml of acetone by stirring for 20 min. The undissolved material was filtered and the filtrate was concentrated to about 15 ml. The pale yellow material thus obtained was recrystallized twice from acetone (200 ml) in the manner described above. It was washed with a small amount of acetone and was dried at room temperature *in vacuo*. Yield, about 0.9 g (63%); mp = 109 to 110°C. Anal: Calcd for $\text{C}_{26}\text{H}_{28}\text{PdClP}$: C, 60.83; H, 5.50; Cl, 6.91; Pd, 20.73%. Found: C, 60.86; H, 5.45; Cl, 6.87; Pd, 20.44%. The molecular weight in CH_2Cl_2 was 529 (calcd: 513). Infrared spectrum: 3080(w), 3060(w), 3030(m), 2940(s), 2920(s), 2895(m), 2855(m), 2845(m), 1590(w), 1575(w), 1485(vs), 1455(w), 1439(vs), 1354(w), 1325(w), 1310(w), 1272(w), 1263(m), 1233(w), 1190(m), 1162(m), 1105(vs), 1077(w), 1035(m), 1022(m), 1005(m), 972(w), 920(w), 855(w), 831(w), 780(w), 768(s), 752(vs), 706(vs), 699(vs), 623(w), 539(vs), 520(vs), 503(vs), 465(m),

435(m), 290(m) (vs = very strong, s = strong, m = medium, w = weak).

3. *Analysis of reaction mixtures and isolation of reaction intermediates.* The samples withdrawn during the reactions were extracted with petroleum ether (bp 30–60°C) (50 ml) and were concentrated to a small volume. After filtration, the filtrates were analyzed by glc analysis. The precipitates obtained by the above procedure dissolved partially in acetone, and the undissolved materials were recrystallized from chloroform. The acetone solution was concentrated to a small volume until crystals appeared. They were recrystallized several times until a pure compound having a constant elemental analysis and sharp melting point or decom-

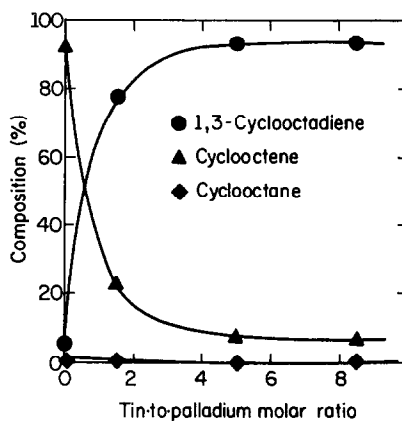


FIG. 1. Effect of SnCl_2 -to-catalyst ratio in the catalytic hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ at 90°C. Results measured after 5.0 hr; hydrogen pressure = 51 atm; solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); catalyst = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmole.

TABLE 1
Hydrogenation of 1,5-Cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ in Various Solvents at 90°C^a

Expt	Solvent ^b	Added compound in reaction solution	Reaction time (hr)	Composition of product (%) ^c		
				1,3-Cyclo- octadiene	Cyclo- octene	Cyclo- octane
1	CH_2Cl_2		5.0	40	58	2
2	CH_2Cl_2	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}^d$	5.0	82	18	0
3	$\text{CH}_2\text{Cl}_2(4) + \text{CH}_3\text{OH}(1)$		5.0	4	93	3
4	$\text{CH}_2\text{Cl}_2(4) + \text{CH}_3\text{OH}(1)$	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}^d$	5.0	93	7	0
5	CH_3OH		3.0	2	73	25
			5.0	0	52	48
6	CH_3COOH		3.0	12	82	6
			5.0	0	81	19
7 ^e	CH_3COOH	SnCl_2^f	5.0	90	10	0
8	C_6H_6		5.0	35	51	14
9	CHCl_3		5.0	14	72	14
10	CH_3COCH_3		5.0	10	65	25
11	$\text{C}_6\text{H}_6(3) + \text{CH}_3\text{OH}(2)$		3.0	2	87	11
			5.0	0	81	19
12 ^g	$\text{C}_6\text{H}_6(3) + \text{CH}_3\text{OH}(2)$	SnCl_2^f	5.0	12	88	0

^a $[\text{PdCl}_2(\text{P}\phi_3)_2] = 0.63$ mmole, 1,5-cyclooctadiene = 9.24 mmoles, under 51 atm of hydrogen.

^b Solvent = 50 ml; () represents volume ratio of mixed solvents.

^c All the products contain trace amount of bicyclo[3.3.0]oct-2-ene except for Expts 7 and 12.

^d $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} = 5.27$ mmoles.

^e Data from H. Itatani and J. C. Bailar, Jr., *Ind. Eng. Chem. Prod. Res. Develop.* 11, 146 (1972).

^f $\text{SnCl}_2 = 5.27$ mmoles.

^g Data at 100°C.

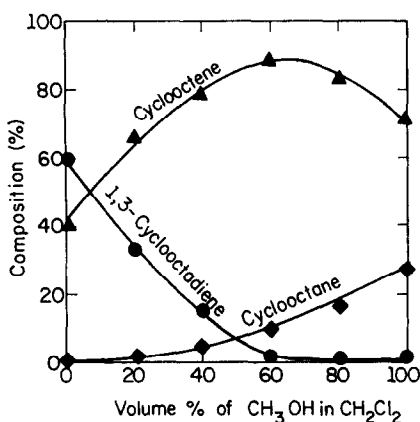


FIG. 2. Effect of CH_3OH on the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ at 90°C . Results measured after 3.0 hr; catalyst = 0.63 mmole; solvent = 50 ml; 1,5-cyclooctadiene = 9.24 mmole; hydrogen pressure = 51 atm.

position point was obtained. Following the above procedure, a compound having chemical and physical properties identical with that of the complex $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ synthesized above was obtained.

RESULTS AND DISCUSSION

Reaction conditions in the selective hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$. Figure 1 shows the effect of SnCl_2 on the selective hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ in $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{OH}(4:1)$ at 90°C . The smaller the ratio, SnCl_2/Pd , the faster the reaction. High selectivity as regards the formation of cyclooctene is observed in all reactions. Table 1 shows the solvent effect on the hydrogenation of 1,5-cyclooctadiene. Table 1 also indicates that SnCl_2 poisons the hydrogenation of 1,5-cyclooctadiene in other solvents, too. Thus, these results clearly indicate that SnCl_2 acts as a poison in the case of the homogeneous $[\text{PdCl}_2(\text{P}\phi_3)_2]$ catalyst, and these results parallel those for the heterogeneous Pd(II) catalyst (16).

As seen in Table 1, the catalytic activity

and selectivity depend to a remarkable degree on the nature of the solvent. CH_2Cl_2 , $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{OH}(4:1)$, and CH_3COOH are good with regard to both the catalytic activity and selectivity. The reduction in CH_3OH is the fastest but least selective. Other solvents such as C_6H_6 , CHCl_3 , CH_3COCH_3 , and $\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}(3:2)$ are somewhat poor in selectivity. A similar solvent effect has already been found in the heterogeneous Pd(II) system, too (16). Figure 2 shows the effect of CH_3OH on the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ in CH_2Cl_2 . The addition of CH_3OH makes the reaction faster, but it makes the selectivity much lower. However, since the selectivity at the CH_3OH content of 20% is still high, we used the 4:1 mixture of CH_2Cl_2 and CH_3OH as a solvent.

Figure 3 shows the effect of the olefin: catalyst ratio on the hydrogenation of 1,5-cyclooctadiene. Both the catalytic activity and selectivity are quite high even when the ratio is very large, and the reactivity is close to that of the heterogeneous Pd(II) catalyst (16).

Table 2 indicates the temperature de-

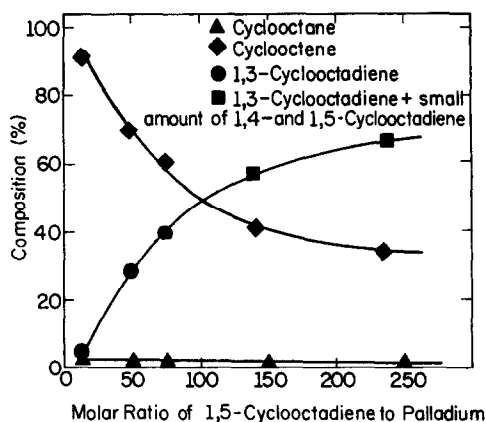


FIG. 3. Effect of the olefin: catalyst ratio on the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ at 90°C . Results measured after 5.0 hr; hydrogen pressure = 51 atm; solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); catalyst = 0.63 mmole.

TABLE 2
Temperature Dependence on the Selective Hydrogenation of 1,5-Cyclooctadiene
with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ in $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{OH}$ (4:1)^a

Expt	Temp (°C)	Reaction time (hr)	Composition of product (%)					
			1,5-Cyclo- octadiene	1,4-Cyclo- octadiene	1,3-Cyclo- octadiene	Cyclo- octene	Cyclo- octane	Bicyclo- [3.3.0]- oct-2-ene
13	27	7.0	72	Tr	6	15	7	Tr
14	57	7.0	33	10	20	22	15	Tr
15	71	7.0	0	0	29	59	12	Tr
16	90	3.0	0	0	32	67	1	Tr
		5.0	0	0	4	93	3	Tr
17	118	0.5	0	0	0	99	1	Tr
		3.0	0	0	0	94	6	Tr
18 ^b	150	0.5	0	0	0	90	1	3

^a $[\text{PdCl}_2(\text{P}\phi_3)_2] = 0.63$ mmole; 1,5-cyclooctadiene = 9.24 mmoles; solvent = 50 ml; hydrogen pressure = 51 atm.

^b Unknown material was detected.

pendence on the selective hydrogenation of 1,5-cyclooctadiene. It is seen that the higher the temperature, the higher the selectivity. But, above about 90°C, the catalyst gradually decomposes to give a small amount of palladium black. Since the palladium black is formed after the concentration of dienes becomes negligibly small, the reaction with palladium black can be neglected. Moreover, the reaction at 150°C produces an unknown material which has a higher boiling point than that of 1,5-cyclooctadiene. Thus, we carried out our experiments at 90°C to make the formation of the palladium black as small as possible and to make the selectivity as high as possible. Here, it is interesting that, although the isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene is much faster than the formation of cyclooctene at temperatures over 70°C, not only in $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{OH}$ (4:1), but also in the other solvents mentioned above, the reduction of 1,5-cyclooctadiene is faster than the isomerization at room tempera-

ture. This means that there exists at least two different reaction mechanisms. This is discussed in detail below.

The degree of hydrogenation was independent of pressure in the range of 13.6 to 51.0 atm of hydrogen. At atmospheric pressure, however, the hydrogenation is very slow.

Isolation of the reaction intermediate. All the hydrogenation solutions of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ at 90°C show color changes during the reactions: immediately after hydrogen gas is introduced, the color of the solution is yellow and $[\text{PdCl}_2(\text{P}\phi_3)_2]$ can be recovered in high yield (80–90%). At this stage, 1,5-cyclooctadiene forms about 70 to 90% of all the olefins. In the middle of the reaction, the color is pale yellow and pale yellow material ($[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$) and $[\text{PdCl}_2(\text{P}\phi_3)_2]$ were isolated in about 60 and 30% yields, respectively. At this point, the content of 1,5-cyclooctadiene is very small and, as the experiment continues, 1,3-cyclooctadiene forms about 80

to 30% of the olefins. When the content of 1,3-cyclooctadiene becomes less than about 20%, the color of the solution changes to a dark yellow or orange and $[\text{PdCl}_2(\text{P}\phi_3)_2]$ can be recovered again in high yield (70–80%). The color then changes to red and then to dark red or brown. From the red solution, a reddish powder is obtained, but it is quite unstable and, during the recrystallization, it easily decomposes to form $[\text{PdCl}_2(\text{P}\phi_3)_2]$, a black precipitate, and dark red unknown material. When the hydrogenation experiment was carried out without an olefin, the color of the solution turned from yellow to red, and then dark red. Similar color changes are observed for both the hydrogenation solutions of the pale yellow material with and without olefin. Since the red color appears after the content of cyclooctadienes becomes negligibly small and it also appears in the hydrogenation solutions containing no olefin, the red color and the dark red color are apparently not directly related to the hydrogenation of cyclooctadienes. On the other hand, the pale yellow material is more active than $[\text{PdCl}_2(\text{P}\phi_3)_2]$, as mentioned below.

From the elemental analysis and mol-

ecular weight measurements, the formula of the pale yellow material is determined to be $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$. Since this compound can also be prepared by using 1,3-cyclooctadiene, the C_8H_{13} group may be the 2-cycloocten-1-yl anion. Although the PMR spectrum is somewhat broad, by decoupling, the peak assignment can be performed as shown in Fig. 4. The signal of olefin proton *trans* to $\text{P}\phi_3$ shifts to a lower field as compared with that of the one at the *cis* position (18). In the case of $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$, the signal of H(3) shifts down to about 5.4 ppm and overlaps with that of H(2). The small $J_{1,2}$ and $J_{2,3}$ values between olefin protons indicate *cis* couplings. In fact, the molecular model suggests that H(1), H(2), and H(3) take the *cis*, *cis*-configuration in the cyclic cyclooctenyl system. Since this PMR spectrum is quite similar to those of $[\text{PdCl}(\pi\text{-allyl})(\text{P}\phi_3)]$ (18), a π -allyl structure can be assigned to the complex. The complex, $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$, is somewhat stable in the solid state, but less stable in solution; it gradually decomposes to form palladium black and $[\text{PdCl}_2(\text{P}\phi_3)_2]$. The addition of excess triphenylphosphine to a CDCl_3 solution of $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$

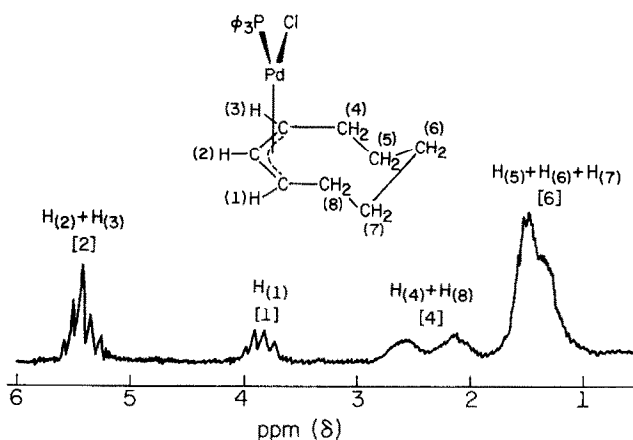


FIG. 4. PMR spectrum of $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$ in CDCl_3 . [] represents the number of protons. $\text{H}(1)$: $\delta = 3.85$ ppm, $J_{1,2} = \text{ca. } 6.9$ Hz; $J_{1,8} = \text{ca. } 6.8$ Hz; $\text{H}(2)$: $\delta = 5.41$ ppm; $J_{2,3} = \text{ca. } 6.9$ Hz; $\text{H}(3)$: $\delta = 5.39$ ppm; $J_{3,\text{P}} = \text{ca. } 9.6$ Hz; $J_{3,4} = \text{ca. } 6.9$ Hz.

TABLE 3
 Hydrogenation of 1,5-Cyclooctadiene with $[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]^a$

Expt	Temp (°C)	Time (hr)	Added compound in reaction solution (mmole)	Composition of product (%) ^b				
				1,5-Cyclo-octadiene	1,4-Cyclo-octadiene	1,3-Cyclo-octadiene	Cyclo-octene	Cyclo-octane
19	27	1.5		17	Tr	5	71	6
		2.5		2	Tr	4	75	18
20	90	1.5		0	0	36	61	2
		3.0		0	0	10	83	6
21 ^c	90	1.5		0	0	Tr	65	34
22	27	1.5	$\text{P}\phi_3$, 0.8	84	Tr	1	13	2
		3.0		72	Tr	2	22	4
23	90	1.5	$\text{P}\phi_3$, 0.8	Tr	Tr	70	28	1
		3.0		0	0	40	58	1
		5.0		0	0	6	91	2
24	90	1.5	$\text{P}\phi_3$, 3.3	3	Tr	85	11	1
		3.0		0	0	70	28	1
		5.0		0	0	49	48	2
25	27	1.5	$(\text{CH}_3)_4\text{NCl}$, 3.3	20	Tr	7	70	3
		3.0		2	Tr	5	84	11
26	90	1.5	$(\text{CH}_3)_4\text{NCl}$, 3.3	Tr	Tr	40	58	1
		3.0		0	0	14	81	4
27	90	3.0	$\text{P}\phi_3$, 0.8	0	0	31	68	1
		5.0	$\text{P}\phi_3$, 0.8 + $(\text{CH}_3)_4\text{NCl}$, 3.3	0	0	2	96	2

^a Catalyst = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmoles; solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); hydrogen pressure = 34 atm.

^b All the products contain small amounts of bicyclo[3.3.0]oct-2-ene (Tr = 1%).

^c Solvent = CH_3OH (50 ml).

makes the PMR spectrum complicated and $[\text{PdCl}_2(\text{P}\phi_3)_2]$ is precipitated from the solution.

Catalytic activity of $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$. Data for the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}(\pi\text{-cyclooc-$

tenyl)($\text{P}\phi_3$)] under various reaction conditions are summarized in Table 3. For comparison, data for the other catalysts are listed in Tables 4 and 5. Data for the hydrogenation of 1,3-cyclooctadiene are shown in Table 6.

 TABLE 4
 Effects of Chloride Ion and Triphenylphosphine on the Hydrogenation of 1,5-Cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]^a$

Expt	Temp (°C)	Time (hr)	Added compound in reaction solution (mmole)	Composition of product (%) ^b		
				1,3-Cyclo-octadiene	Cyclo-octene	Cyclo-octane
28	90	3.0	$\text{P}\phi_3$, 3.3	73	25	2
		5.0		46	51	3
29	90	3.0	$(\text{CH}_3)_4\text{NCl}$, 3.3	33	67	0
		5.0		2	96	2

^a Solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); $[\text{PdCl}_2(\text{P}\phi_3)_2]$ = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmoles; hydrogen pressure = 34 atm.

^b Product contains trace amount of bicyclo[3.3.0]oct-2-ene.

TABLE 5
 Hydrogenation of 1,5-Cyclooctadiene with $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]_a$

Expt	Temp (°C)	Time (hr)	Added compound in reaction solution (mmole)	Composition of product (%) ^b				
				1,5-Cyclo- octadiene	1,4-Cyclo- octadiene	1,3-Cyclo- octadiene	Cyclo- octene	Cyclo- octane
30 ^c	27	0.5		4	0	Tr	13	83
		1.5		0	0	0	2	98
31 ^c	90	0.5		0	0	0	11	89
		1.5		0	0	0	Tr	99
32	27	1.5	$\text{P}\phi_3$, 0.8	26	Tr	5	57	12
		3.0		8	Tr	3	70	19
33	90	1.5	$\text{P}\phi_3$, 0.8	0	0	38	58	4
		3.0		0	0	13	78	9
34	90	1.5	$\text{P}\phi_3$, 3.3	0	0	73	25	2
		3.0		0	0	48	49	2
		5.0		0	0	10	88	2
35 ^c	90	0.5	$(\text{CH}_3)_4\text{NCl}$, 3.3	0	0	0	18	82
		1.5		0	0	0	4	96

^a Catalyst = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmoles; solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); hydrogen pressure = 34 atm.

^b Products in Expts 32, 33, and 34 contain trace amount of bicyclo[3.3.0]oct-2-ene.

^c The reaction solution contains a large amount of Pd-black ppt.

From the experiments 19, 20 (Table 3) and 13, 16 (Table 2), it is seen that $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ is much more reactive than $[\text{PdCl}_2(\text{P}\phi_3)_2]$, not only at 90°C, but also at 27°C. In the case of the hydrogenation at 90°C, the isomerization is faster than the reduction, but the reduction is faster than the isomerization at 27°C. This is confirmed by the fact that the reduction of 1,3-cyclooctadiene at 27°C is somewhat slow compared with that of 1,5-cyclo-

octadiene at 27°C (Expt 37 in Table 6). The selectivity is quite high at 90°C, but it is somewhat low at 27°C. This behavior of $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ as regards the temperature dependence is quite similar to that of $[\text{PdCl}_2(\text{P}\phi_3)_2]$.

Experiments 22–27 (Table 3) and 28, 29 (Table 4) show the effects of chloride ion and triphenylphosphine on the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ and $[\text{PdCl}_2(\text{P}\phi_3)_2]$. An

 TABLE 6
 Hydrogenation of 1,3-Cyclooctadiene^a

Expt	Catalyst	Temp (°C)	Time (hr)	Composition of product			
				1,3-Cyclo- octadiene	Cyclo- octene	Cyclo- octane	Bicyclo- oct-2-ene
36	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	3.0	29	70	1	Tr
			5.0	2	97	1	Tr
37	$[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$	27	1.5	35	64	1	0
			3.0	15	82	3	0
38	$[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$	90	1.5	31	68	1	Tr
			3.0	6	89	5	Tr

^a Catalyst = 0.63 mmole; 1,3-cyclooctadiene = 9.24 mmoles; solvent = CH_2Cl_2 (40 ml) + CH_3OH (10 ml); hydrogen pressure = 34 atm.

excess of chloride ion effects no great change in the composition of the reaction product and the rate of the reaction, but an excess of triphenylphosphine gives a remarkable change in the rate of the reaction. The rates of the reactions with $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ are very close to that with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ when about 1 mole of excess triphenylphosphine is added (Expts 22 and 23). When 5 moles of excess of triphenylphosphine are added, the reactions become pretty slow with both catalysts. These similarities in chemical properties between $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ and $[\text{PdCl}_2(\text{P}\phi_3)_2]$ indicate that $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ is the important reaction intermediate in the selective hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$. The effect of methanol is also very similar for both catalysts (Expts 21, 23, 3, and 5).

Table 5 shows the results of the hydrogenation of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{1,5-cyclooctadiene})]$. The catalyst is extremely active, but shows no selectivity by itself. However, when more than 1 mole of excess of triphenylphosphine is added to the reaction solution, the catalyst shows high selectivity and its reactivity is quite close to those of $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ and $[\text{PdCl}_2(\text{P}\phi_3)_2]$.

From the above experimental facts, it is seen that 1 mole of triphenylphosphine/mole of Pd(II) is inevitably necessary for the selectivity of the catalyst, but more than 1 mole of triphenylphosphine is generally not required. In the case of the heterogeneous Pd(II) polymer catalyst, although it has more than 2 moles of $-\text{CH}_2\text{P}\phi_2$ group/Pd(II) (16), the reactivity is quite similar to that of $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ rather than to that of $[\text{PdCl}_2(\text{P}\phi_3)_2]$. It is known that the addition of a trace amount of triphenylphosphine to the polymer catalyst poisons its reactivity strongly and that the corresponding monomer $[\text{PdCl}_2(\phi_2\text{PCH}_2\phi)_2]$ is a poor catalyst (16, 19). Therefore, the high reactivity of the polymer catalyst may come from steric properties. That is, the pair of $-\text{CH}_2\text{P}\phi_2$ groups may not be able to act as a strong complexing agent due to steric hindrance in the complicated polymer chain.

Reaction mechanism. Table 7 shows the isomerization of 1,5-cyclooctadiene with $[\text{PdCl}_2(\text{P}\phi_3)_2]$ and $[\text{PdCl}(\pi\text{-cyclo-octenyl})(\text{P}\phi_3)]$ under a nitrogen atmosphere. In all the cases, practically no hydrogenation occurs. Thus, hydrogen is necessary for the hydrogenation. On the other hand, the

TABLE 7
Isomerization of 1,5-Cyclooctadiene under Nitrogen Atmosphere^a

Expt	Catalyst	Temp (°C)	Solvent	Composition of product (%)				
				1,5-Cyclo-octadiene	1,4-Cyclo-octadiene	1,3-Cyclo-octadiene	Cyclo-octene	Cyclo-octane
39	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	CH_2Cl_2	69	18	13	0	0
40	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	CH_3OH	52	13	35	0	0
41	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	$\text{CH}_2\text{Cl}_2(4)$ + $\text{CH}_3\text{OH}(1)$	50	15	35	0	0
42 ^b	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	— ^b	96	4	0	0	0
43 ^{b,c}	$[\text{PdCl}_2(\text{P}\phi_3)_2]$	90	— ^b	13	40	28	16	3
44 ^d	$[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$	90	$\text{CH}_2\text{Cl}_2(4)$ + $\text{CH}_3\text{OH}(1)$	7	5	85	3	0
45	$[\text{PdCl}(\text{C}_8\text{H}_{13})(\text{P}\phi_3)]$	27	$\text{CH}_2\text{Cl}_2(4)$ + $\text{CH}_3\text{OH}(1)$	100	0	0	0	0

^a Catalyst = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmoles, under nitrogen (34 atm) for 3.0 hr; solvent = 50 ml.

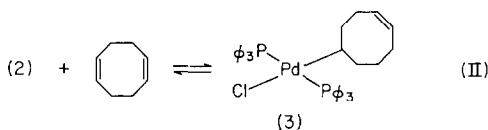
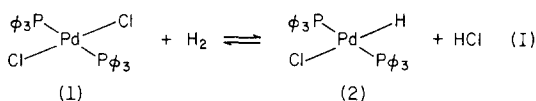
^b 92.4 mmoles of 1,5-cyclooctadiene was used.

^c Under 34 atm of hydrogen.

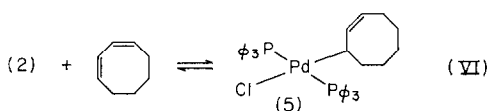
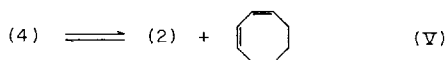
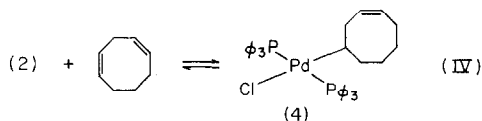
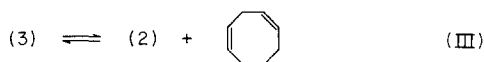
^d The product contains a trace amount of bicyclo[3.3.0]oct-2-ene.

isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene is observed under nitrogen at 90°C. In the case of $[\text{PdCl}_2(\text{P}\phi_3)_2]$, however, the rate is negligibly slow compared with that under hydrogen. But, in the case of $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$, the isomerization rate is almost as fast as that under hydrogen. These facts suggest that the isomerization occurs mainly by way of a partly hydrogenated diolefin anion complex.

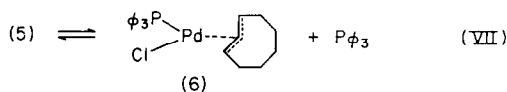
Recently, hydride complexes such as $[\text{Pd}(\text{H})\text{Cl}(\text{PET}_3)_2]$ (20) and $[\text{Pd}(\text{H})\text{Cl}(\text{P}\phi_3)_2]$ (21) have been reported. Although the hydride complex, $[\text{Pd}(\text{H})\text{Cl}(\text{P}\phi_3)_2]$, could not be isolated from the hydrogenation solutions of $[\text{PdCl}_2(\text{P}\phi_3)_2]$, it was observed that $[\text{PdCl}_2(\text{P}\phi_3)_2]$ becomes soluble in various organic solvents and produces HCl when the complex is hydrogenated. Thus, the first step of the hydrogenation reaction should be the formation of the hydride complex (2) followed by addition of 1,5-cyclooctadiene to form 4-cycloocten-1-yl complex (3):



Then, the isomerization of 1,5-cyclooctadiene may occur by similar reactions such as III, IV, V, and VI:

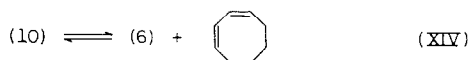
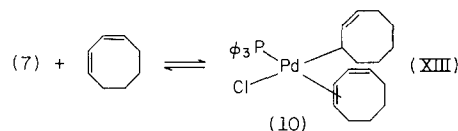
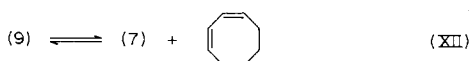
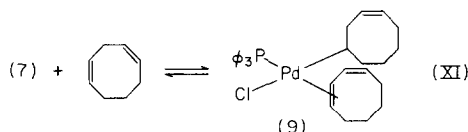
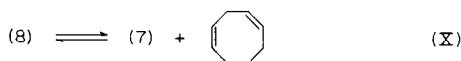
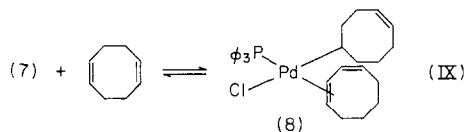
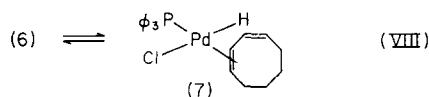


And, $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ (6) may be formed by the dissociation of one mole of $\text{P}\phi_3$ from complex (5):



Many reactions similar to VII have been reported for $[\text{PdCl}(\text{allyl})(\text{P}\phi_3)]$ and $[\text{PdCl}(\text{allyl})_2]$ (22).

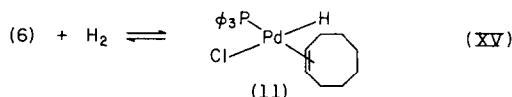
However, $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ itself is active for the isomerization; thus, the following similar reactions such as VIII to XIV may also occur after the formation of complex (6):



In reactions VIII to XIV, we considered that π -olefin and $\text{P}\phi_3$ behave as strong π -acid ligands (23).

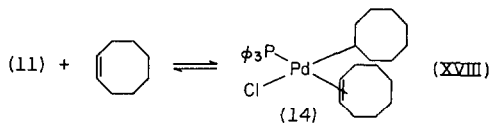
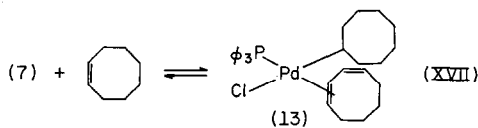
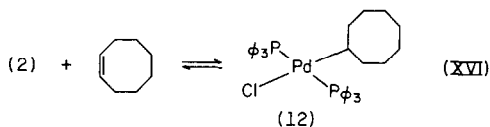
If hydrogen is present, reaction (XV)

may occur:



and the isomerization may also occur through complex (11) in a similar manner to those shown in reactions VIII to XIV.

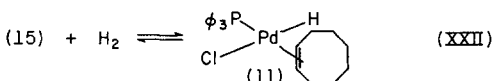
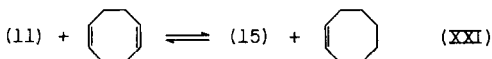
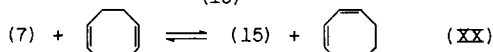
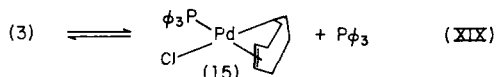
It has been observed that the formation of cyclooctene becomes slower when an excess of $\text{P}\phi_3$ is added to the reaction solution. This suggests that the reduction of olefin occurs mainly through complex (6) and not through complexes which contain 2 moles of $\text{P}\phi_3$ such as (3), (4), and (5). Moreover, we have observed the formation of bicyclo[3.3.0]oct-2-ene in almost all the reactions carried out above 90°C . This gives strong support to the hypothesis that the hydrogenation occurs by way of a π -allylic intermediate as has been reported in the case of $[\text{NiI}_2(\text{P}\phi_3)_2]$ catalyst (14). Therefore, reactions such as XVI, XVII, and XVIII may also be possible, but no further hydrogenation will occur:



The above explanation is limited to reactions at higher temperatures because, at room temperature, the reduction of 1,5-cyclooctadiene is faster than the isomerization.

In the reaction at room temperature, the reduction of 1,5-cyclooctadiene with $[\text{PdCl}(\pi\text{-cyclooctenyl})(\text{P}\phi_3)]$ is quite rapid. However, if an excess of $\text{P}\phi_3$ is present in the reaction solution, the reaction becomes

extremely slow (Expts 19 and 22 in Table 3). In order to explain these facts, we assume the formation of a sigma-pi-4-cycloocten-1-yl intermediate (15) and think that the reduction can occur from this complex at room temperature.



Sigma-pi-4-cycloocten-1-yl Pd(II) complexes similar to (15) have been reported (17, 24). Although the isomerization to 1,3-cyclooctadiene is very slow at room temperature, 1,3-cyclooctadiene is also reduced to cyclooctene (Expt 37). Thus, reaction XV should be considered in this case, too. At higher temperature, complex (15) may be too unstable to contribute to the reaction.

Table 8 shows the effect of hydrogen chloride on the hydrogenation of 1,5-cyclooctadiene. It is observed that hydrogenation occurs even under hydrogen chloride. When both hydrogen and hydrogen chloride are present, the reaction becomes faster than that under pure hydrogen. The effect of hydrogen chloride is especially marked at 90°C . It has been shown that methanol behaves as a hydrogen source in the hydrogenation of olefin with a Pd(II) catalyst containing SnCl_2 (5). Although no hydrogenation is observed in CH_3OH or in $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{OH}$ (4:1) under nitrogen (Expts 40, 41, 44, and 45 in Table 7), methanol may become the hydrogen source when HCl is present.

The reaction under hydrogen chloride produces a small amount of an unknown material which has a higher boiling point than that of 1,5-cyclooctadiene. The same unknown material is also observed in the reaction at 150°C (Expt 18), and in the

TABLE 8
Effect of Hydrogen Chloride on the Hydrogenation of 1,5-Cyclooctadiene^a

Expt	Catalyst	Gas	Material added to reaction solution (mmole)	Time (hr)	Composition of product (%)				
					1,5-Cyclo-octadiene	1,4-Cyclo-octadiene	1,3-Cyclo-octadiene	Cyclo-octene	Cyclo-octane
46 ^{b,c}	[PdCl ₂ (Pφ ₃) ₂]	N ₂	HCl, 20	3.0	0	0	63	35	Tr
				5.0	0	0	33	64	Tr
47 ^b	[PdCl ₂ (Pφ ₃) ₂]	H ₂	HCl, 7.5	1.5	0	0	27	70	3
				3.0	0	0	0	92	8
48 ^b	[PdCl ₂ (Pφ ₃) ₂]	H ₂	HCl, 30	1.5	0	0	25	73	2
				3.0	0	0	1	95	4
49 ^d	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	N ₂	HCl, 20	3.0	72	Tr	11	17	0
50 ^{b,e}	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	N ₂	HCl, 20	3.0	0	0	35	64	0
51 ^d	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	H ₂	HCl, 20	3.0	11	2	5	74	8
52 ^{b,e}	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	H ₂	HCl, 20	3.0	0	0	4	89	6
53 ^{b,e}	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	N ₂	HCl, 20	3.0	Tr	Tr	82	13	Tr
54 ^{b,f}	[PdCl(C ₈ H ₁₃)(Pφ ₃)]	N ₂	HCl, 20	1.5	0	0	35	65	0

^a Catalyst = 0.63 mmole; 1,5-cyclooctadiene = 9.24 mmoles; solvent = CH₂Cl₂ (40 ml) + CH₃OH (10 ml); under 34 atm hydrogen or nitrogen at 90°C; all the reaction solutions are green.

^b The product contains a trace amount of bicyclo[3.3.0]oct-2-ene.

^c The product contains a trace amount of unknown material.

^d Data at 27°C.

^e The product contains about 4% of unknown material.

^f Data for hydrogenation of 1,3-cyclooctadiene.

reaction with [PdCl(π-cyclooctenyl)(Pφ₃)] at 110°C when an excess of (CH₃)₄NCl is present.

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