The Codimerizations of Styrene with Vinyl Compounds Catalyzed by Olefin-palladium(II) Chloride Complexes

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The codimerization of styrene with vinyl compounds catalyzed by di-μ-chloro-dichlorobis(styrene)dipalladium(II), $(Pd(C_6H_5CH{=}CH_2)Cl_2)_2$, was investigated in a homogeneous system under mild conditions. The reaction of styrene and methyl acrylate carried out at 50°C for 6 hr yielded 220% codimers, 169% dimers of methyl acrylate, and 18% dimers of styrene, on the basis of the palladium(II) used. The codimerizations of styrene with vinyl acetate and with methyl vinyl ketone gave 50% codimer and 125% codimers respectively. When nitroethylene and *n*-butyl vinyl ether were used as the vinyl compound, no codimers were formed. The codimerization of styrene-d_3 with ethylene was also carried out. The reaction mechanism involving the five-coordinate hydridopalladiumolefin intermediate was proposed and discussed in the terms of the distribution of deuterium in the codimer of styrene-d_3 and ethylene, the functional group effects of vinyl compounds, and solvent effects on the codimerization.

Many investigations have recently been reported for the cooligomerizations of conjugated dienes with mono-olefins catalyzed by transition-metal compounds. Few reports have appeared, however, concerning the codimerizations of simple olefins with vinyl compounds and the dimerizations of vinyl compounds.[1]

As has been reported in a preliminary communication,[2] we have found that olefin-palladium chloride complexes are an effective catalyst for the codimerization of styrene with ethylene. Afterwards, Barlow and his co-workers reported the dimerizations and the codimerizations of olefins catalyzed by a benzonitrile palladium chloride complex and suggested that the palladium hydride is an intermediate.[3] The investigations of the substituent effects of vinyl compounds and the structure of codimers on codimerization reactions give an important suggestion as to the reaction mechanism of the oligomerizations of olefins. In this paper, the codimerization of styrene with various vinyl compounds will be investigated. A reaction mechanism involving the five-coordinate hydridopalladium-olefin intermediate will be proposed and discussed in the terms of the functional group effects of vinyl compounds and solvent effects on the codimerization.

Experimental

Codimerization of Styrene with Vinyl Compounds. A reaction vessel was charged with 10.7 mmol of a styrene-palladium complex, 0.7 mol of styrene, and 0.7 mol of a vinyl compound; then, the mixture was stirred at 50°C for 6 hr. This solution thereby turned reddish-brown. The resulting solution was diluted with petroleum ether after the unreacted reagents had been removed under reduced pressure at 50°C; then it was filtered to remove the catalyst and palladium metal. The filtrate was distilled under reduced pressure. The products were separated by distillation or preparative-glcg, and were identified by infrared spectroscopy (Jasco model IR-E), proton magnetic resonance spectroscopy (JNM-4H-100 and JNM-C60HL), mass spectrometry (Hitachi RMS-4 mass spectrometer), and elemental analysis.

Methyl *trans*-5-phenyl-4-pentenoate: IR spectrum: C=O 1735 cm^{-1}, *trans*-HC=CH–963 cm^{-1}, phenyl 747 and 695 cm^{-1}. NMR spectrum: CH_3 τ 6.39 (s), CH_2 τ 7.58 (m), –HC=CH– τ 3.61 (d) and 3.89 (m), phenyl τ 2.78 (m). Found: C, 76.12; H, 7.55%. Calcd for $C_{12}H_{14}O_2$; C, 75.76; H, 7.42%.

Methyl *trans*-2-methyl-4-phenyl-3-butenoate: IR spectrum: C=O 1735 cm^{-1}, *trans*-HC=CH– 966 cm^{-1}, phenyl 749 and 699 cm^{-1}. NMR spectrum: CH_3 τ 6.36 (s) and 8.68 (d), CH τ 7.50 (m), –HC=CH– τ 3.58 (d) and 3.83 (m), phenyl τ 2.78 (^{6}).

Methyl *trans*-5-phenyl-3-pentenoate: IR spectrum: C=O 1735 cm^{-1}, *trans*-HC=CH– 966 cm^{-1}, phenyl 749 and 699 cm^{-1}. NMR spectrum: CH_3 τ 6.36 (s), CH_2 τ 6.70 (m) and 6.95 (m), –HC=CH– τ 4.38 (m), phenyl τ 2.78 (m).

trans-1-Phenyl-4-acetoxy-1-butene: IR spectrum: C=O 1735 cm^{-1}, *trans*-HC=CH– 967 cm^{-1}, phenyl 748 and 696 cm^{-1}. NMR spectrum: CH_3 τ 8.04 (s) CH_2 τ 5.91 (m) and 7.53 (q), –HC=CH– τ 3.57 (d) and 3.92 (m), phenyl τ 2.79 (m).

trans-1-Phenyl-4-acetyl-1-butene: IR spectrum: C=O 1712 cm^{-1}, *trans*-HC=CH– 967 cm^{-1}, phenyl 752 and 697 cm^{-1}. NMR spectrum: CH_3 τ 7.94 (s), CH_2 τ 7.54 (m), –HC=CH– τ 3.63 (d) and 3.91 (m), phenyl τ 2.81 (m).

Methyl *trans*-3-pentenoate: NMR spectrum: CH_3 τ 6.38 (s) and 8.31 (d), CH_2 τ 7.06 (m), –HC=CH– τ 4.50 (m).

Methyl *trans*-2-pentenoate: IR spectrum: C=O 1730 cm^{-1}, *trans*-HC=CH– 981 cm^{-1}. NMR spectrum: CH_3 τ 6.33 (s) and 8.91 (t), CH_2 τ 7.75 (m), –HC=CH– τ 3.04 (m) and 4.24 (d).

Codimerization of Styrene-d_3 *with Ethylene.* Styrene-d_3 was prepared using the method described by Kirchner.[4] Mixtures of acetophenone (25 g), 99.75% D_2O (30 m*l*), and 40% NaOD in D_2O (0.3 m*l*) were stirred at 85°C for 10 hr. The resulting solutions gave 98% acetophenone-d_3 (23 g) when the same procedure was repeated three times. The reduction of acetophenone-d_3 with $LiAlD_4$ (4 g) gave $C_6H_5CD(OH)CD_3$ (20.5 g). The alcohol was dehydrated using

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[1] a) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965). b) H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem. Intern. Ed.*, **4**, 327 (1965). c) A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *Chem. Commun.*, **1967**, 357. d) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, This Bulletin, **43**, 877 (1970).

[2] K. Kawamoto, T. Imanaka, and S. Teranishi, *Kogyo Kagaku Zasshi*, **72**, 1612 (1969).

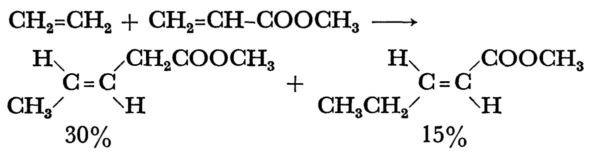
[3] M. G. Barlow, M. J. Bryant, R. N. Hanszeldine, and A. G. Mackie, *J. Organometal. Chem.*, **21**, 215 (1970).

[4] K. Kirchner, *Makromol. Chim.*, **96**, 179 (1966).

the method of Overberger *et al.*[5] to give styrene-d_3 (12.5 g). From the analysis of the integral curve of the NMR spectrum, assuming the phenyl protons to be 5H, the α and β protons of styrene were found to contain 0.02H and 0.04H respectively. A glass autoclave was charged with an ethylene-palladium complex (1.5 g) and styrene-d_3 (10 g). The autoclave was flushed with ethylene and pressured to 4 atm, and then the mixture was stirred at 50°C for 6 hr. From the NMR spectrum analysis of the codimer thus obtained, assuming the phenyl protons to be 5H, it was calculated that olefinic methynyl, saturated methylene, and methyl protons in *trans*-1-phenyl-1-butene contained 0.97H, 0.78H, and 0.98H respectively. The estimated error in the observed values of the protons was *ca.* 0.02H.

Results and Discussion

The codimerization reaction of styrene with ethylene reported in a preliminary communication[2] was applied to the system of ethylene and methyl acrylate with a functional group. Ethylene was bubbled into a methyl acrylate solution containing an ethylene-palladium chloride complex catalyst at 50°C for 6 hr. The following products were thus obtained:



(based on palladium(II))

Methyl acrylate also could be successfully codimerized with ethylene. However, the yield is rather low because ethylene dissolves slightly in methyl acrylate under atmospheric pressure; therefore, the codimerization reactions of styrene instead of ethylene with various vinyl compounds were investigated.

The codimerization reactions of styrene with vinyl compounds catalyzed by the styrene-palladium chloride complex were carried out at 50°C for 6 hr. The results are shown in Table 1. The codimerization reaction of styrene with methyl acrylate gave not only the codimers of styrene and methyl acrylate, but also the dimers of methyl acrylate. When the other polar vinyl compound were used, no dimers of polar vinyl compounds were formed. Though the codimerization rate of styrene with vinyl acetate is slow, the complex remains as a stable catalyst for at least 6 hr. As is shown in Table 1, it was found that the codimers obtained as the main products have a linear structure in which the β carbon of styrene is bonded to the β carbon of the vinyl compound, with a shifting of the hydrogen on the β carbon of styrene. The relation between the functional groups on vinyl compounds and the yields of the codimers is shown in Table 2. When methyl acrylate bearing a carbomethoxy group is used as the vinyl compound, the best yield of codimers is obtained; the yield decreases in the following sequence: $-CO_2CH_3>-COCH_3>-OCOCH_3$. When nitroethylene, which has a strongly electron-withdrawing group, and *n*-butyl vinyl ether, bearing a *n*-butoxy group which is an electron-donating group are used, no codimer has been formed. When nitroethylene is used as the vinyl compound, we obtained a stable yellow-brown precipitate which shows the presence of phenyl and nitro groups in its infrared spectrum. When *n*-butyl vinyl ether is used, a viscous solution containing a higher polymer of *n*-butyl vinyl ether whose infrared spectrum shows the presence of a C–O–C bond is instantaneously formed.

TABLE 2. RELATION BETWEEN FUNCTIONAL GROUPS OF VINYL COMPOUNDS(CH_2=CH–X) AND YIELD OF CODIMERS

X	$-NO_2$	$-\underset{\underset{O}{\parallel}}{C}-CH_3$	$-\underset{\underset{O}{\parallel}}{C}-O-CH_3$	$-O-\underset{\underset{O}{\parallel}}{C}-CH_3$	$-OC_4H_9$
Yield[a], %	—	125	220	50	—

a) Yields are based on the catalyst used.

The dependence of the concentration of vinyl compounds on the rates of the codimerization reactions of styrene with methyl acrylate and with vinyl acetate is shown in Fig. 1. The rate of the codimerization of styrene with methyl acrylate is proportional to the concentration of methyl acrylate in a high concentration of styrene and is independent of the concentrations of the reactants in a high concentration of methyl acrylate, because the styrene-palladium chloride complex has been used as a catalyst and the rate of the codimerization was

TABLE 1. REACTION OF STYRENE AND VINYL COMPOUNDS

Vinyl compound	Products[a]
CH_2=CH–CO_2CH_3	*trans*-C_6H_5CH=$CH(CH_2)_2CO_2CH_3$, 190%; *trans*-$C_6H_5CH_2CH$=$CHCH_2CO_2CH_3$, 10%. *trans*-C_6H_5CH=$CHCH(CH_3)CO_2CH_3$, 20%. *trans*-CH_3O_2CCH=$CH(CH_2)_2CO_2CH_3$, 153%; *trans*-$CH_3O_2CCH_2CH$=$CHCH_2CO_2CH_3$, 16%. Dimers of styrene[b], 18%.
CH_2=CH–$OCOCH_3$	*trans*-C_6H_5CH=$CH(CH_2)_2OCOCH_3$, 50%. Dimers of styrene,[b] 32%.
CH=CH–$COCH_3$	*trans*-C_6H_5CH=$CH(CH_2)_2COCH_3$, 18%; isomers of codimer,[c] 107%. Dimers of styrene,[b] 14%.

Styrene-palladium complex (Pd): 10.7 mmol, styrene: 0.7 mol, vinyl compound: 0.7 mol. 50 C, 6 hr.
a) Yields are based on the catalyst used.
b) Four isomers of dimer of styrene containing *trans*-1,3-diphenyl-1-butene.
c) Three isomers of codimer of styrene with methyl vinyl ketone which were identified by infrared spectrum.

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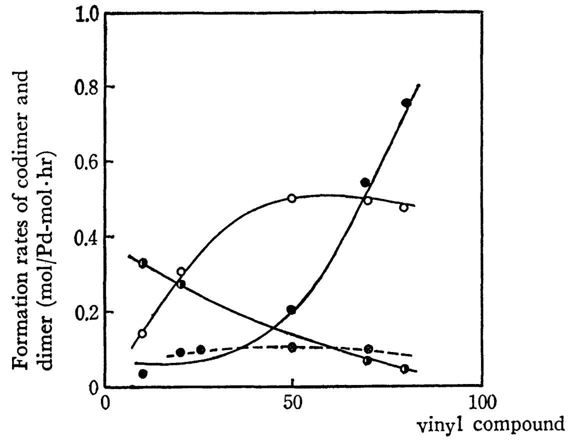
[5] C. G. Overberger and J. H. Saunders, "Org. Syn.," Coll. Vol. 3, p. 204.



Concentration of vinyl compound(mol%)

Fig. 1. The dependence of the concentration of vinyl compounds on the formation rates of codimerization and dimerization reactions.

○: Codimer of styrene with methyl acrylate, ●: dimer of methyl acrylate, ◐: dimer of styrene, ⊗: codimer of styrene with vinyl acetate. Styrene-palladium complex (Pd): 10.7 mmol, styrene+vinyl compound: 0.94 mol, nitromethane: 0.47 mol. 50°C.

measured at the point where codimers were formed in an equal amount of the catalyst used. The dimerization rates of styrene and methyl acrylate increase with increases in the styrene and methyl acrylate concentrations respectively, and the increase in the dimerization rate of methyl acrylate is larger than that in the dimerization rate of styrene. An induction period has been observed in the dimerization of methyl acrylate, but not in the dimerization of styrene; this may result from the use of the styrene-palladium complex as a catalyst. The rate of the codimerization of styrene with vinyl acetate is smaller than that of styrene with methyl acrylate and is not remarkable dependent upon the concentration of the reactants.

The solvent effect on the codimerization of styrene with methyl acrylate and on the dimerization of methyl acrylate is summarized in Table 3.[6] The formation ratio of the codimer to the dimer does not remarkably depend on the solvents except in the case of acetic acid. As was observed in the dimerization of ethylene and in the codimerization of styrene with ethylene in previous papers,[7,8] the reaction rate is enhanced in solvents containing the oxygen atom, such as phenol, nitromethane, and nitrobenzene. The reaction rate is larger in systems without a solvent than in acetic acid and benzene solvents. It appears that the reactant itself is a good solvent. Since the solvent effect was not observed in benzene on the dimerization of ethylene[7] or on the codimerization of styrene with ethylene,[8] benzene is deduced to play a role in diluting the catalytic solution. On the other hand, in contrast with the rate of the codimerization of styrene with methyl acrylate, the rate of the dimerization of methyl acrylate in acetic acid is lower than that in benzene. Since acetic acid is a good solvent in the dimerization of ethylene[7] and in the codimerization of styrene with ethylene[8], and since the dimer of styrene in acetic acid is formed in more than 3 mol equivalents of that in systems without a solvent, it may be suggested that acetic acid disturbs the coordination of methyl acrylate to the catalyst through some interactions between acetic acid and methyl acrylate.

Table 3. Solvent effects on the codimerization of styrene with methyl acrylate and on the dimerization of methyl acrylate

Solvent	Formation rate of codimer (mol/ Pd-mol·hr)	Formation rate of dimer (mol/ Pd-mol·hr)	Dielectric constant[6] ε(°C)
Phenol	0.530	0.311	6.15(20)
Nitromethane	0.495	0.192	22.7(10)
Nitrobenzene	0.431	—	34.8(25)
Dioxane	0.304	0.118	2.28(0)
Non solvent	0.218	0.103	—
Acetic acid	0.197	0.035	9.78(60)
Benzene	0.109	0.063	2.44(0)

Styrene-palladium complex (Pd): 10.7 mmol, styrene: 0.47 mol, methyl acrylate: 0.47mol, solvent: 0.47 mol. Reaction temperature: 50°C.

Furthermore, when the codimerization of styrene-d_3 with ethylene was carried out at 50°C for 6 hr, the results were as follows:

$$CH_2{=}CH_2 + C_6H_5CD{=}CD_2 \longrightarrow$$
$$CH_{2.02}D_{0.98}\text{-}CH_{1.22}D_{0.78}\text{-}\underbrace{CH{=}CH}_{H:D=1.03:0.97}\text{-}C_6H_5$$

This experimental evidence on the distribution of deuterium can be interpreted according to the following scheme:[9]

$$CH_2{=}CH_2 + C_6H_5CD{=}CD_2 \longrightarrow CH_2{=}CH\text{-}CD_2\text{-}CHD\text{-}C_6H_5$$
$$\longrightarrow CH_2D\text{-}CH{=}CD\text{-}CHD\text{-}C_6H_5 \longrightarrow$$
$$CH_2D\text{-}CHD\text{-}CH{=}CD\text{-}C_6H_5 \text{ and } CH_2D\text{-}CH_2\text{-}CD{=}CD\text{-}C_6H_5$$

The codimerization reactions of styrene with vinyl compounds have the following characteristic features: (i) the use of methyl acrylate as a vinyl compound gives more codimers than that of the other vinyl compounds; (ii) the codimers produced as main products have a linear structure in which the β carbon of styrene is bonded to the β carbon of vinyl compound *via* a hydrogen shift of the β carbon of styrene; (iii) this reaction is enhanced in solvents containing the oxygen atom, particularly in weak dissociated solvents and in strongly polar solvents such as nitrobenzene, and (iv) the use of nitrobenzene or dioxane as solvent which can not be considered to be hydride sources makes it easy to give the codimer. The codimerization reaction includes the following two processes: (a) the coordina-

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[6] Chem. Soc. Japan, "Kagaku Binran, Kisohen I(Chem. Table, Basic I)," Maruzen, Tokyo (1966), p. 1003.

[7] K. Kawamoto, T. Imanaka, and S. Teranishi, *Nippon Kagaku Zasshi*, **91**, 39 (1970).

[8] K. Kawamoto, T. Imanaka, and S. Teranishi, This Bulletin, **43**, 2512 (1970).

[9] Harrod and his co-workers reported that the palladium complexes isomerize the olefins by a C_3—C_1 hydrogen shift in the isomerization of 1-heptene-3-d_3.[10]

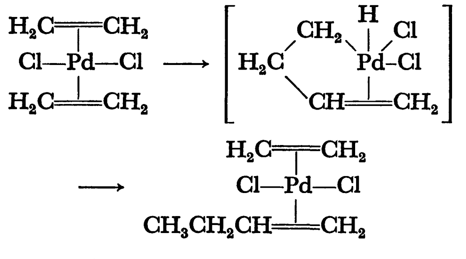
[10] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **88**, 3491 (1966).

tion reaction includes the following two processes: (a) the coordination of the vinyl compound to the palladium ion, and (b) the hydrogen shift between the coordinated styrene and the vinyl compound. An electron-withdrawing property of the functional groups decreases in the following order on the basis of Hammett's σ value:[11]

$-NO_2 > -COCH_3 > -CO_2CH_3 > -OCOCH_3 >$ Phenyl $> n$-butoxy

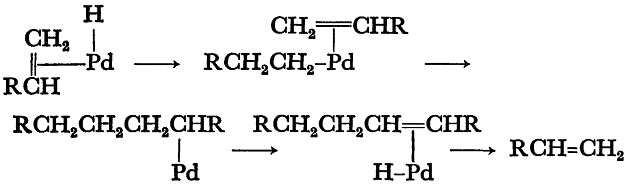
If the π-bond formation between olefins and the palladium (II) ion depends predominantly on the back-donation of filled d-electrons in the palladium ion, the π-bonding ability of the vinyl compound to the palladium ion will decrease with a decrease in the σ value. On the other hand, since hydrogen is easily bonded to most transition metals as a hydride, the ease with which the hydride is formed from the coordinated vinyl compound is the opposite of the order of the σ values. It may be assumed that the best yield of the codimer when methyl acrylate is used in the codimerization of styrene with vinyl cmpounds is derived from these two opposite components.

Recently, Ketley *et al.* have suggested the following mechanism for the palladium-catalyzed dimerization of ethylene;[12]

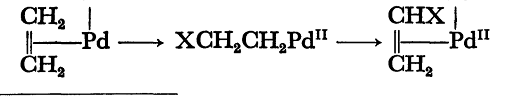


This mechanism can not, however, account for the main process of the dimerization reaction of ethylene, namely, the insertion reaction, because the carbon atom of the ethylene π-bonded to palladium has a partially positive charge, unlike free ethylene, and so the insertion reaction between π-bonded ethylenes can not be expected. It can also not account for the remarkable effect of the solvents described above.

Barlow *et al.* have reported a mechanism of the dimerization of olefins which involves the formation of the palladium hydride as a catalytic active species:[3]

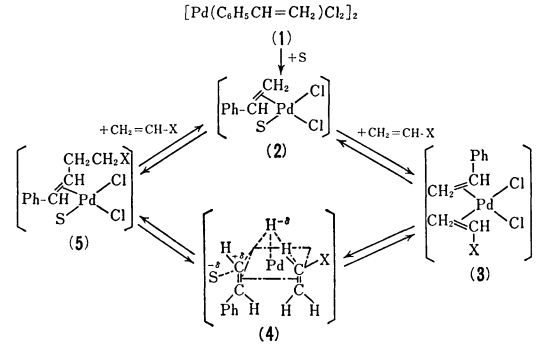


The hydrogen of the initially-formed Pd^{II}–H has been described as resulting from the solvents or the olefins as is shown in the following scheme:



However, this mechanism, assuming the Pd^{II}–H to be a catalytic active species, can not reasonably account for the following facts: (a) styrene and vinyl compounds readily codimerize in systems without a solvent or in such solvents as nitrobenzene and dioxane, which can not be considered to be hydride sources; (b) analysis of the reaction solutions by glcg show no trace of the corresponding halogenated compound, and (c) in the experiment of the codimerization of styrene-d_3 with ethylene, if ethylene and styrene-d_3 are codimerized by Pd^{II}–H and Pd^{II}–D without any exchange reaction of Pd^{II}–H and Pd^{II}–D in the isomerization, the expected products are CH_3–CH_2–CD=CD–C_6H_5 and mixtures of CH_3–CHD–CD=CH–C_6H_5 and CH_3–CHD–CD=CD–C_6H_5 or of CH_2D–CH_2–CD=CD–C_6H_5 and CH_3–CHD–CD=CD–C_6H_5. These results are different from this experimental evidence. On the other hand, the presence of the exchange reaction of Pd^{II}–H and Pd^{II}–D in every stage of the isomerization gives mixtures of numerous products in which deuterium is distributed in various ways. Therefore, the ratio of hydrogen to deuterium in the methyl group of the codimer can be expected to be higher than 2 in the Pd^{II}–H mechanism; the observed ratio was found to be approximately 2 in this experiment. We are inclined to believe that the codimerization proceeds through a reaction path which requires no external source of hydride.

On the basis of the above facts (i)—(iv) and the results of the codimerization reaction of styrene-d_3 with ethylene, we wish to propose the reaction mechanism, with a hydride shift between coordinated styrene and vinyl compound, shown in Scheme 1.[13]



Scheme 1

The styrene-palladium complex (1) initially dissociates into a complex (2) in the presence of a solvent. The coordination of the vinyl compound with the complex (2) results in another complex (3). In the stage of the insertion reaction from the complex (3) to the complex (5) *via* an intermediate (4), the palladium ion easily abstracts the β carbon of styrene as a hydride rather than the vinyllic hydrogen of the vinyl compound, with an electron-withdrawing group, thus reforming the five-coordinate hydridopalladium-olefin intermediate (4). This hydride is added to the α carbon of the vinyl compound with the electron-withdrawing

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[11] J. Hine, "Physical Org. Chem.," Mcgrew-Hill, N. Y. (1956), p. 65.

[12] A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

[13] K. Kawamoto, T. Imanaka, and S. Teranishi, *Nippon Kagaku Zasshi*, **89**, 639 (1968).

group to the four-coordinate palladium-alkyl complex and then, this alkyl group is inserted into the partially-positive β carbon of styrene, thus reforming the complex (5) through the coordination of the solvent to a vacant coordination site. The codimerization reaction may proceed by repeating these processes. A nucleophilic approach of the solvent can facilitate the abstraction of a hydride from styrene by the palladium ion and stabilize the partially-positive β carbon of styrene. These functions of the solvent were suggested by Volger in the oxidative dimerization of β-substituted α-olefins by palladium acetate.14) Recently, Fackler *et al.* have reported ascertaining the presence of the five-coordinate complex by nuclear magnetic-resonance spectroscopy in reactions of xanthates and dithiocarbamates of palladium (II) and platinum (II) with methyldiphenylphosphine15) while Tayim *et al.* have proposed a reaction mechanism involving the five-coordinate complex as an intermediate in the isomerization catalyzed by the platinum complexes.16) In addition to the function of the solvent described above, the solvent may catalytically keep the coordination site active through its coordination in the stage of changing from the complex (3) to the complex (5) and may also accelerate the coordination of the vinyl compound through its dissociation in the stage of changing from the complex (2) to the complex (3). The same argument was previously made by the present authors in attempting to explain the dimerization of ethylene7) and the codimerization of styrene with ethylene.8)

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14) H. C. Volger, *Rec. Trav. Chim.*, **86**, 677 (1967).

15) J. P. Fackler, Jr., W. C. Seidel, and John A. Fetchin, *J. Amer. Chem. Soc.*, **90**, 2707 (1968).

16) H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 3420 (1967).