

Reactions of Allenes. V.^{*1)} The Reaction of Allene with Palladium Salts^{*2)}

Tadashi OKAMOTO*

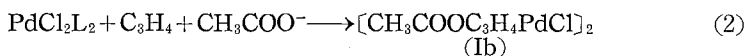
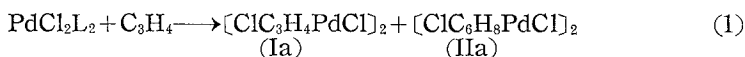
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The reaction of allene with palladium salts has been studied by the use of dichlorobis-(benzotrile)palladium and palladium acetate. The effects of solvent and reaction temperature on the product distribution were examined with $(C_6H_5CN)_2PdCl_2$. From the reaction of allene with palladium acetate, a 2,2'-bi- π -allyl complex was isolated besides the reported complexes. The mechanism of the reaction has been discussed based on the obtained results. The effect of solvent has been explained by the back bonding ability of the solvent molecule, and the assistance of insertion reaction by the back bonding ligand has been proposed.

INTRODUCTION

In the course of an investigation of organometallic compounds using allene, the author has reported palladium complexes having an allene trimer ligand and some results on the structure and the reactivity of π -allylic palladium complexes.¹⁾ In the present investigation, the reaction of allene with palladium(II) salts leading to π -allylic complexes was investigated to obtain the information on the mechanism of the reaction.

It is well known that the reaction of allene with palladium chloride yields two π -allylic palladium complexes^{*3)} in various ratios mainly depending on the solvent used; di- μ -chlorobis(2-chloro- π -allyl)dipalladium (Ia) and di- μ -chlorobis{2-[1-(chloromethyl)viny]- π -allyl}dipalladium (IIa) (Eq. 1).^{2,3)}



(L = Cl⁻ or C₆H₅CN)

It was also reported that in acetic acid containing acetate ion, di- μ -chlorobis(2-acetoxy- π -allyl)dipalladium (Ib) was obtained exclusively (Eq. 2).⁴⁾ As to the effect of solvent on these reactions, it was explained at first that IIa was formed in polar solvents and Ia was produced in nonpolar solvents.^{2,3)} Afterwards the

* 岡本 忠: Laboratory of Organic Unit Reactions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

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*3 The formation of a mixed complex, di- μ -chloro(2-chloro- π -allyl){2'-[1'-(chloromethyl)viny]- π' -allyl}dipalladium, had been described in a literature.²⁾ But it was partly separated into Ia and IIa by recrystallization, and hence it was treated as a mixture of Ia and IIa in this paper.

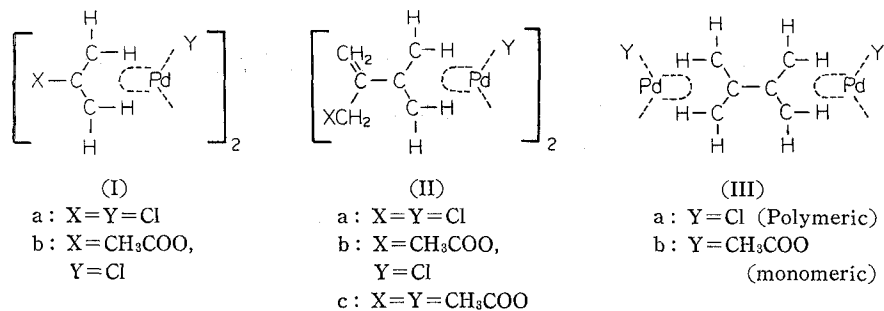
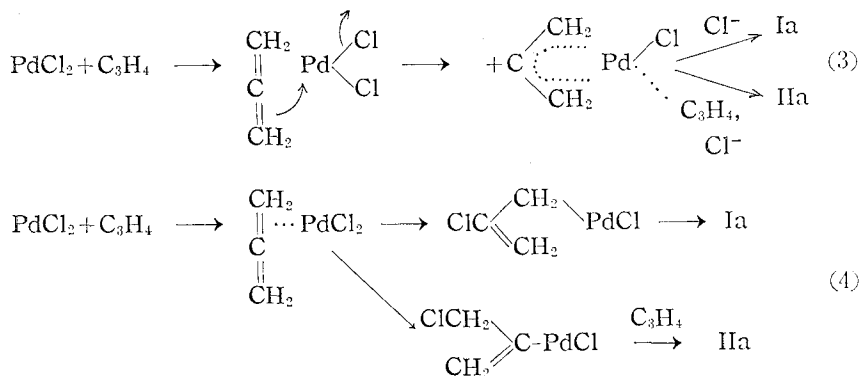


Fig. 1. The structure of the complexes.

solvation of the free anion in solution by protic solvent was suggested, and they proposed that the reaction proceeded through a nucleophilic substitution of chloro ligand by allene and a subsequent attack of another molecule of allene and/or a nucleophile at the cationic central carbon of a co-ordinated allene (Eq. 3).^{4,5)} Another mechanism proposed independently by Heck⁶⁾ was the insertion of allene into a Pd-Cl bond (Eq. 4).



We tried the reaction in ten solvents and examined the effect of temperature. Palladium acetate was also used for the substrate. The mechanism of the reaction is discussed based on the obtained results and a reaction path is proposed for the reaction. The effect of solvent is explained by the back bonding ability of the solvent molecule.

RESULTS

Reaction of Allene with Dichlorobis(benzonitrile)palladium. The effect of solvent on the distribution of Ia and IIa is shown in Table 1. In the most polar solvent, nitrobenzene, the main product was complex Ia, which had been reported to predominate in nonpolar solvents. As for ether, the main product was IIa in tetrahydrofuran, and Ia was formed predominantly in anisole. Among the halogenated hydrocarbons, the chlorides, except chlorobenzene, preferred IIa, while dibromomethane did Ia. The proportion of IIa increased with

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 Table 1. Influence of the Solvent on the Product Distribution.^{a)}

Solvent	D. C. ^{b)}	Yield ^{a)} (%)	Product Distribution (mol %)		Lit.
			I a	II a	
Nitrobenzene	35.75	93	68	32	
Methanol	33.5	>88	—	100 ^{b)}	5
Benzonitrile	25.58	79	—	100	4
Benzonitrile ^{d)}		44	51	49	
<i>o</i> -Dichlorobenzene	9.82	67	—	100	
Dichloromethane	9.14	76	39	61	
Tetrahydrofuran	7.58	79	29	71	
Dibromomethane	7.04	94	65	35	
Chlorobenzene	5.64	90	67	33	
Chloroform	4.81	86	29	71	
Anisole	4.41	85	65	35	
Toluene	2.38	87	78	22	
Benzene	2.28	89	76	24	

a) $(C_6H_5CN)_2PdCl_2$: 300 mg, solvent: 18 ml, allene: 200 ml, room temperature.

b) Dielectric constants at 20°C.

c) Calculated on the basis of the complex used.

d) Carbon monoxide was bubbled before introducing allene. The other product was IIIa (28% based on the complex used).

e) Contained di- μ -chlorobis{2-[1-(methoxymethyl)vinyl]- π -allyl}dipalladium.

increasing chlorine atoms in the solvent molecule. The presence of aromatic ring seemed to favor the formation of Ia. In the presence of carbon monoxide, equal amounts of Ia and IIa were produced in benzonitrile, which is a solvent selective for IIa. Further investigation was restricted by the low solubility of dichlorobis(benzonitrile)palladium in solvents such as ethyl acetate, ethyl acrylate, *m*-dichlorobenzene, anilin, carbon tetrachloride, acetonitrile, and *n*-butyl ether.

The effect of the reaction temperature on the product distribution is shown in Table 2. The chief product of the reaction of allene with dichlorobis(benzonitrile)palladium in toluene was Ia at 30°C, but IIa was formed mainly at -30°C.

 Table 2. Influence of the Reaction Temperature on the Product Distribution.^{a)}

Temp (°C)	Reaction Time (min)	Yield ^{b)} (%)	Product Distribution (mol %)	
			I a	II a
30	3	87	78	22
0	14	84	41	59
-30	300	88	14	86

a) $(C_6H_5CN)_2PdCl_2$: 300 mg, toluene: 18 ml, allene: 200 ml.

b) Based on the amount of palladium complex used.

Reaction of Allene with Palladium Acetate. As was reported preliminarily,⁷⁾ the reaction of allene and palladium acetate, followed by the treatment of the

Table 3. Reaction of Allene with Palladium Acetate.^{a)}

Run	Reaction Time (min)	I b	Product (%) ^{b)} II b	III b
1	12	2	4	12
2	80	13	49	16
3	360	14	26	12
4 ^{c)}	12	—	2	—
5 ^{d)}	12	—	31	7

a) Palladium acetate: 1.0 g, benzene: 50 ml, allene: 300 ml, room temperature.

b) Based on the amount of the palladium species used.

c) Benzene: 100 ml, allene: 600 ml.

d) One-quarter of the palladium source was added in the form of IIc. The yield of IIb included the amount derived from charged IIc (25 %).

resulting solution with aqueous sodium chloride, yielded complex Ib and di- μ -chlorobis{2-[1-(acetoxymethyl)viny]- π -allyl}dipalladium (IIb). It was further found that dichloro-2, 2'-bi- π -allyldipalladium (IIIa) was also formed in this reaction as an insoluble precipitate. The results are shown in Table 3.^{*4)} In Table 3, the yield of di- μ -acetato-2, 2'-bi- π -allyldipalladium (IIIb), obtained by the treatment of IIIa with silver acetate, was listed instead of IIIa, because the isolation of IIIa was difficult on account of its low solubility in most solvents. These chloro complexes obtained by the treatment with aqueous sodium chloride were considered as resulting from the exchange of the acetato ligands in the complexes for chloride ion. The presence of di- μ -acetatobis{2-[1-(acetoxymethyl)viny]- π -allyl}dipalladium (IIc) in the reaction mixture was detected by NMR spectrum, but the isolation of the acetato complexes from it was unsuccessful, possibly because of their instability.⁹⁾ The decrease in the yields at a long reaction time (360 min in Run 3) indicates some decomposition of the resulting acetato complexes during the reaction, and the reproducibility of the reaction was not so good. It is clear, however, that complex IIb was obtained in a larger amount than Ib. The almost constant yields of IIIb in Runs 1-3 suggest that IIIb was obtained in the early stage of the reaction. In Runs 4 and 5, the effect of the reaction conditions on the formation of IIIb was studied. When the initial concentration of palladium acetate was reduced to a half, about a half amount of IIa was obtained, but IIIb was not obtained in the same reaction time (Run 4 compared with Run 1). In Run 5, a part (one-quarter) of the amount of palladium acetate used in Run 1 was replaced by IIc. If IIIb is produced by the reaction of IIc with palladium acetate, the yield of IIIb in Run 5 would increase relative to the yield in Run 1. The result indicated that the yield was lower than the value in Run 1.

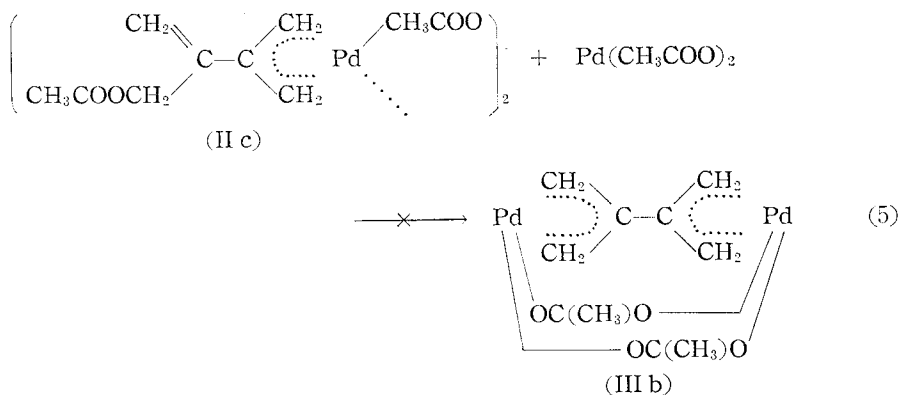
*4 It seems strange that di- μ -chloro[2, 2'-(1-methyleneethylene)bis- π -allyl]dipalladium was not produced in these reactions. It was true even if a larger amount of allene was used. The result might be explained by the dissociation of μ -acetato bridges of complex IIIb in the reaction mixture, resulting a loss of strain which is considered to be a driving force for insertion.⁸⁾

DISCUSSION

The similarity of the products in the reaction using dichlorobis(benzonitrile)-palladium and palladium acetate suggests that these reactions proceed by the similar mechanism.

The results show that the explanation of solvent effect by polarity is insufficient at least from two points; the predominant formation of Ia in the most polar solvent, nitrobenzene, and the fact that the proportion of IIa is larger in less polar chloroform than in more polar dichloromethane, dibromomethane, and chlorobenzene. Another explanation of the solvent effect by solvation⁴⁾ is difficult to apply to the results in aprotic solvents.

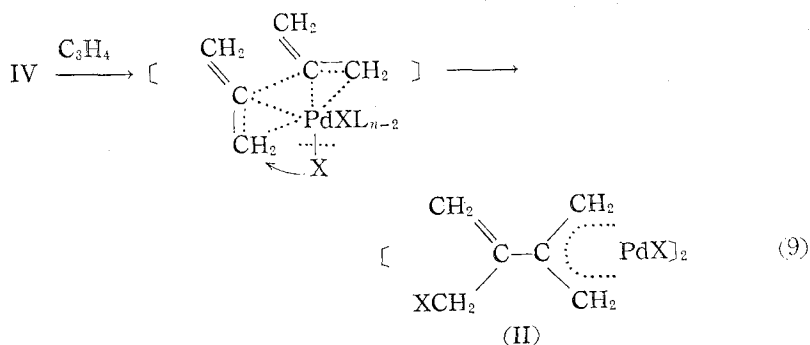
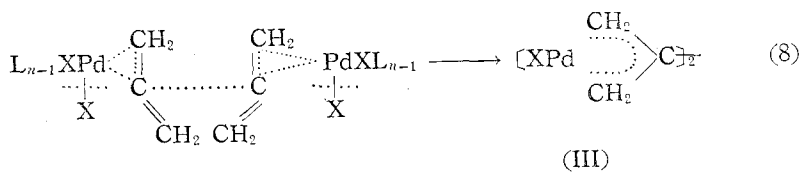
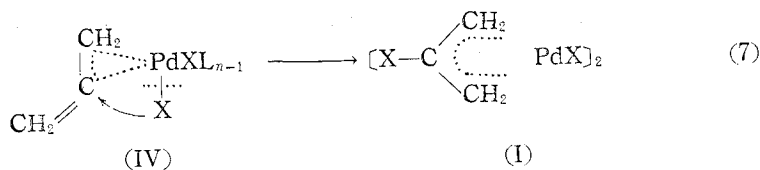
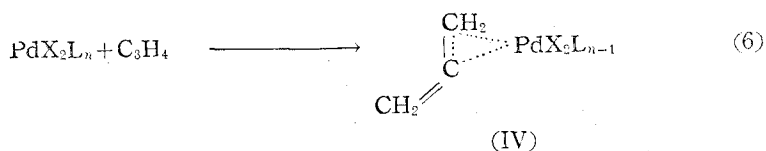
No formation of IIb in the reaction of allene with palladium chloride and sodium acetate reported by Susuki *et al.*⁴⁾ and the formation of IIb with palladium acetate in this study give an argument against the mechanism of Eq. 3. Since chloride ion on the metal is not replaced by acetate ion under their condition,¹⁰⁾ these results suggest that the group X in complex II (see Fig. 1) is derived from X co-ordinated on the metal. A similar reaction to Susuki's one using a half amount of sodium acetate (1.0 g) gave complex IIa in a fair yield (34 %). These discussions suggest that Eq. 3 is not a main path of the reaction. The course may be responsible for the formation of the complex of type I, but it does not account for the formation of II. As for the insertion mechanism suggested by Heck (Eq. 4), this mechanism is not responsible for the formation of the complex of type III, since the reaction path from IIc and palladium acetate was eliminated as was described in the preceding section (Eq. 5).



Thus neither of the previously suggested pathways for the reaction could be responsible for the results described here.

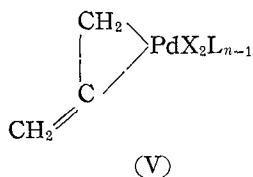
To account for the results, the following pathways are proposed. In the equations, L represents a co-ordinated solvent or such a ligand as benzonitrile.*⁵⁾ The number *n* would not exceed four, but the exact number is unknown.

*5 The influence of benzonitrile initially co-ordinated to the metal is considered to be small as was suggested by Maitlis in the case of the trimerization of acetylenes.¹¹⁾



The first step of the reaction is a co-ordination of allene to the metal (Eq. 6). The resulting π -complex IV reacts to yield π -allylic complexes via insertion (Eq. 7), or via a coupling with another IV (Eq. 8). Further co-ordination of allene to IV yields another π -complex, which rearranges by insertion to yield a complex of type II (Eq. 9).

In the π -complex IV, allene would be reduced to some extent and IV would be partly formulated as V (oxidative addition).^{*6)} Then, such insertion as Eqs. 7 and 9 would be accepted as an intramolecular reductive elimination resulting in the migration of X to the co-ordinated allene.



The coupling of Eq. 8 would be an intermolecular reductive elimination.

*6 As was described by Collman,¹²⁾ the concept of oxidative addition may be an accounting method. One of the physical meanings would be the rehybridization of the ligand orbitals.¹³⁾

It is well known that carbon monoxide, which is a strong back bonding ligand, assists the reductive elimination of π -allylic palladium complexes.^{14,15)} Yamamoto *et al.* also reported lately that back bonding ligands such as some substituted olefins assist the elimination of alkyl radical from alkylnickel complexes.¹⁶⁾ Paying attention to the behavior of solvents as ligands, the solvent effect of this reaction is explained similarly based on the proposed mechanism as follows; the solvents of high or moderate back bonding ability, accelerating solvents, assist the migration of chlorine on palladium to the co-ordinated allene to give complex Ia, and in the solvents of low or no back bonding ability the migration of chlorine does not occur until the second molecule of allene, which is an accelerating ligand with a high back bonding ability, co-ordinates on the metal. This explanation is supported by the result that under the influence of carbon monoxide, about equal amounts of Ia and IIa were obtained even in benzonitrile, which is a selective solvent for IIa. The classification of solvents in the back bonding ability is not sufficiently clear nowadays. Methanol, tetrahydrofuran, and alkyl chlorides have no *d*-orbitals and are classified as donor ligands of no or low ability to accept π -back bonding from metal. Dibromomethane has empty *d*-orbitals and probably accepts some back bonding. It was reported that benzonitrile co-ordinates on Pd or Pt through N-atom,¹⁷⁾ but its donor-acceptor property is not clear. A measurement of an IR spectrum of benzonitrilepentacarbonylchromium showed carbonyl stretching absorptions at 2071, 1951, and 1926 cm^{-1} . These values, being smaller than those of the corresponding acetonitrile complex, reflect the lesser contribution of back bonding for benzonitrile than for acetonitrile,¹⁸⁾ which has slight back bonding ability.¹⁹⁾ The back bonding ability of benzene is also not clear, but it was reported that some back bonding exists in tricarbonylarenechromium.²⁰⁾ In bisarenechromium, it was described that negative charge exists on the ring.²¹⁾ It would not be so rough to classify benzene into ligands being able to accept back bonding moderately. Other aromatic compounds except *o*-dichlorobenzene, for which the chelate effect could be anticipated, would work in the same way as benzene. It is noteworthy that the above classification seems to be similar to the classification of the principle of hard and soft acids and bases proposed by Pearson *et al.*²²⁾

The effect of reaction temperature also supports the proposed mechanism. At lower temperature, the reductive elimination of Cl-atom from chloropalladium complexes, viz. the migration of Cl, would become more difficult, while the coordination of the second molecule of allene, being advantageous for the formation of IIa, is favored. Thus, a high ratio of IIa to Ia would be expected at lower temperature.

Eq. 8 is an intermolecular reaction analogous to the intramolecular reaction proposed in cyclooligomerization of acetylenes,^{23,24)} and accords with the result that a high concentration of palladium acetate favored III b. The result that III was produced only with palladium acetate and not with dichlorobis(benzonitrile)palladium might be concerned with the trimeric structure of palladium acetate in benzene.²⁵⁾

As was described already, some of Ia might be produced by the attack of

an external nucleophile like Eq. 3 and the ratio of Ia : IIa does not fully correspond to the ratio of Eq. 7 : Eq. 9. However, the contribution of Eq. 3 would be small, since the ratio of Ia : IIa appears independent of the nucleophilicity of solvent. In the absence of the nucleophilic attack of Eq. 3 and a coupling of Eq. 8, the ratio of Ia : IIa depends on the facility of the migration of ligand X and the ease of the co-ordination of the second molecule of allene.

EXPERIMENTAL

IR spectra were measured using a Perkin-Elmer 521 spectrophotometer ; NMR spectra, on a Varian A-60 spectrometer for dilute deuteriochloroform solutions with an internal reference of TMS. Solvents were purified by the conventional methods. Palladium acetate and dichlorobis(benzonitrile)palladium were prepared as usual. Allene, carbon monoxide, and other inorganic reagents were obtained commercially and used without further purification.

Reaction of Allene with Dichlorobis(benzonitrile)palladium. In a solvent (18 ml), 300 mg of dichlorobis(benzonitrile)palladium was dissolved. After the atmosphere was replaced by nitrogen, allene gas (200 ml) was introduced at the specified temperature. The mixture was stirred until the color of the solution turned yellow and the resulting solution was evaporated to give a yellow solid, which was washed in hexane (20 ml) to obtain a mixture of Ia and IIa. The ratio of Ia to IIa was determined by the integral ratio of the peaks of NMR at 2.87 and 3.26 ppm. In case of the product being partly insoluble in chloroform as the reaction in the presence of carbon monoxide, the part being soluble in chloroform was treated as above, and the insoluble part was treated by silver acetate in acetone to obtain IIIb.

Reaction of Allene with Palladium Acetate. Palladium acetate (1.0 g) was dissolved in benzene (50 ml), and after replacing the atmosphere with nitrogen, allene gas (300 ml) was introduced. The solution was stirred at room temperature for the specified period, and a saturated aqueous sodium chloride solution (5.0 ml) was added. The resulting mixture was stirred for a while, and then the precipitate was separated from the solution by filtration. The precipitate was washed with water, acetone and dichloromethane, and treated by silver acetate to give IIIb. The filtrate was evaporated to dryness and the residue was recrystallized from dichloromethane-hexane to give a mixture of Ib and IIb. The analysis of the products was performed by NMR.

IR Spectrum of Benzonitrilepentacarbonylchromium. The complex was prepared by the method of Strohmeier *et al.*²⁶⁾ (Found: C, 48.83; H, 1.65; N, 4.82%). The IR spectrum was measured for a 3.1% cyclohexane solution by the use of 19.3 μ sodium chloride cell, and the positions of peaks were checked by the single beam operation.

Isolation and Properties of New π -Allylic Complexes. Complex IIb was isolated from the product described above by the careful recrystallization from dichloromethane-hexane as a yellow crystal, mp 114-116°C (dec).

Found: C, 34.03; H, 4.01%. Calcd for $C_{16}H_{22}O_4Cl_2Pd_2$: C, 34.19; H, 3.95%.

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NMR: δ 2.20 (3H), 2.90 (2H), 4.18 (2H), 4.86 (2H), 5.46 (1H), and 5.86 ppm (1H).

Complex II c was prepared from IIb by the silver acetate method as a yellow crystal, mp 119-121°C (dec).

Found: C, 39.30; H, 4.71%. Calcd for $C_{20}H_{28}O_8Pd_2$: C, 39.47; H, 4.61%.
NMR: δ 2.00 (3H), 2.20 (3H), 2.62 (2H), 3.93 (2H), 4.88 (2H), 5.45 (1H), and 5.70 ppm (1H).

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