Reactions of Allenes. IV.[1] New Palladium Complexes Having a Bridged Allene Trimer Ligand

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Di-μ-acetato-[2,2′-(1-methyleneethylene)bis-π-allyl]dipalladium (I) was obtained (18%) by the reaction of allene and palladium acetate. Its structure was estimated from the data of elemental analysis, molecular weight, hydrogenolysis reaction, IR, and NMR. Complex I was synthesized otherwise by the reaction of allene with di-μ-acetato-2,2′-bi-π-allyldipalladium. The insertion mechanism for the latter reaction was confirmed by the product of the reaction using allene-d_4, $Pd_2(C_9H_8D_4)(CH_3COO)_2$. It was found that this insertion reaction was by far faster than analogous reactions with bis(acetylacetonato)-2,2′-bi-π-allyldipalladium or di-μ-acetato-bis-(π-allyl palladium). The observed acceleration was assumed to be due to strain in the substrate. From NMR data of I and other π-allylpalladium complexes already published, it was shown that the difference in chemical shifts between *syn* and *anti* protons of π-allyl complexes is dependent on the substituents on the central carbon; the non-conjugated substituents give smaller values (0,9—1.01 ppm for μ-chloro complexes), and α,β-unsaturated substituents give larger values (1.27—1.28 ppm for μ-chloro complexes). Chloro and acetylacetonato derivatives of I, and the activation energy for spin exchange of saturated methylene protons in I are also described.

It is well known that an allenic compound produces various stable σ-, π-, and π-allyl complexes by the reaction with transition metal compounds.[2] This suggests that some organometallics affording information on catalytic reactions might be obtained, by the reaction of allene with transition metal compounds which are useful as catalysts in organic syntheses.

On this assumption, the author examined the reaction of allene with palladium acetate, and obtained some new π-allyl complexes.[3,4] This paper deals with a full description of the formation and the structure of the palladium complexes having a new bridging ligand of allene trimer, 2,2′-(1-methyleneethylene)bis-π-allyl. Results are given also on the NMR of the μ-acetato complex with variation of temperature and the fast insertion of allene into a strained π-allyl complex.[4]

Results and Discussion

Isolation and the Structure of Di-μ-acetato-[2,2′-(1-methyleneethylene)bis-π-allyl]dipalladium. Palladium acetate and allene were stirred in benzene overnight. Subsequent separation of the resulting solution with a silica-gel column gave a yellow crystal, di-μ-acetato-[2,2′-(1-methyleneethylene)bis-π-allyl]dipalladium (I). Analytical data and the molecular weight determination showed that the complex had a molecular formula $Pd_2C_{13}H_{18}O_4$. Presence of acetate ligands was estimated by the carboxylate stretching absorptions of its IR spectrum (1570 and 1410 cm^{-1}) and the absorption of acetyl protons (2.0 ppm) on the NMR spectrum. The IR spectrum further showed absence of an ester carbonyl group. This was confirmed by the NMR spectrum of chloro complex VI. Hydrogenolysis of I made it clear that five moles of hydrogen were necessary for complete hydrogenation, and the organic ligand had the carbon framework of 2,3,5-trimethylhexane. At this stage, I was formulated as $Pd_2(C_9H_{12})(CH_3COO)_2$. Further studies of the structure were carried out with the aid of NMR spectra. The spectra are shown in Fig. I. The broad absorptions observed at ambient temperature became sharp at elevated temperatures and the relative intensities of the absorptions became clear; corresponding to the absorptions in the order of decreasing δ value, relative intensities are 1H, 1H, 2H, 2H, 2H, 2H, 2H, and 6H. The spectra are interpreted as consisting of the absorptions by one vinylidene, two π-allyls, and one saturated methylene group from their chemical shifts.[2j,5]

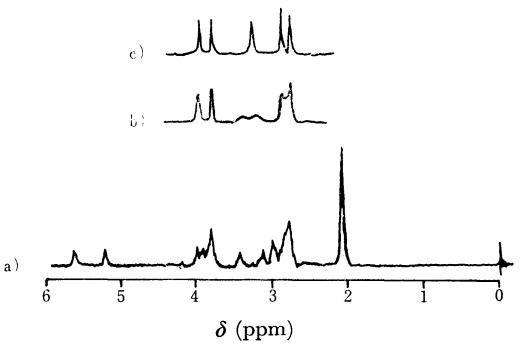


Fig. 1. NMR Spectra of I.
a) in $CDCl_3$ at −28°C.
b) in CD_3COOD at 40°C.
c) in CD_3COOD at 70°C.

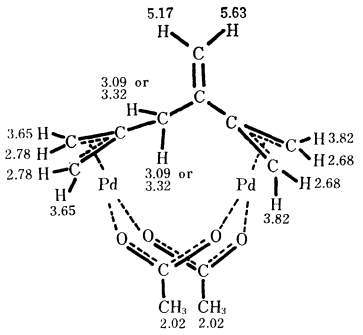
1) Part III: T. Okamoto, S. Kunichika, and Y. Sakakibara, *Bull. Inst. Chem. Res., Kyoto Univ.*, **48**, 96 (1970).

2) For π-complexes: a) J. A. Osborn, *Chem. Commun.*, **1968**, 1231. b) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 2231 (1967). c) P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *Chem. Commun.*, **1969**, 361. d) K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.*, **21**, 467 (1970). For σ-complexes: e) M. Green, N. Mayne, and F. G. A. Stone, *Chem. Commun.*, **1966**, 755. f) R. Ben-Shoshan and R. Pettit, *ibid.*, **1968**, 247. g) S. Otsuka, A. Nakamura, and K. Tani, *J. Organometal. Chem.*, **14**, p 30 (1968). And a). For π-allyl complexes: h) A. Nakamura, This Bulletin, **39**, 543 (1966). i) R. G. Schultz, *Tetrahedron*, **20**, 2809 (1964). j) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc., A*, **1966**, 1687. k) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **20**, p 17 (1969). l) T. Susuki and J. Tsuji, This Bulletin, **41**, 1954 (1968). And f).

3) T. Okamoto, Y. Sakakibara, and S. Kunichika, This Bulletin, **43**, 2658 (1970).

4) T. Okamoto, *Chem. Commun.*, **1970**, 1126.

5) K. Nukada, O. Yamamoto, and T. Suzuki, *Anal. Chem.*, **35**, 1892 (1963).



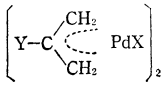
Formula. Structure and NMR Assignment of I (δ value in CD_3COOD at 40°C).

They were supported also by the spectra of the deuterated complex. The structure elucidated from the NMR spectra and their assignments are shown in Formula. The assignments of four absorptions of two π-allyl groups are of interest. An interpretation that the deshielding effect caused by a neighboring unsaturated bond gives higher δ values for the π-allyl group adjacent to a carbon-carbon double bond is not correct. For complex I, the absorptions by the isolated π-allyl appear inside the two absorptions by the π-allyl adjacent to an unsaturated bond. In other words, the difference in chemical shifts between the absorptions by *syn* and *anti* protons of a π-allyl group,

$$\Delta\delta = \delta_{syn} - \delta_{anti}$$

is larger for the π-allyl group adjacent to an unsaturated bond than for the isolated π-allyl. This seem to be the general rule at least for palladium complexes. For di-

TABLE 1. NMR DATA OF π-ALLYLIC PALLADIUM COMPLEXES



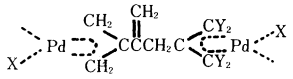
(in $CDCl_3$, ppm down-field from TMS)

Complex	δ_{anti}	δ_{syn}	$\Delta\delta$	Literature
X=Cl				
Y=H–	3.09	4.07	0.98	6
Y=Cl–	3.26	4.27	1.01	2j
Y=CH_3–	2.88	3.85	0.97	6
Y=CH_3COO–	3.10	4.00	0.90	2l
Y=CH_3CH_2COO–	3.12	4.04	0.92	2l
Y=CH_2=C(CH_2-Cl)–	2.87	4.15	1.28	
Y=CH_2=C(CH_2-OCH_3)–	2.83	4.10	1.27	2i
Y=CH_2=C(CH_2-$OCOCH_3$)–	2.90	4.18	1.28	
X=CH_3COO				
Y=H–	2.85	3.88	1.03	6
Y=CH_3–	2.71	3.70	0.99	6
Y=$C_3H_4C(=CH_2)$-CH_2–[a]	2.78	3.65	0.87	
Y=CH_2=C(CH_2-$OCOCH_3$)–	2.62	3.93	1.31	
Y=CH_2=C-($CH_2C_3H_4$)–[a]	2.68	3.82	1.14	

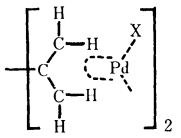
a) The values for complex I.

6) S. D. Robinson and B. L. Shaw, *J. Organometal. Chem.*, **3**, 367 (1965).

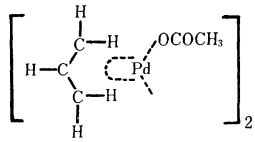
μ-chloro dipalladium complexes, an isolated π-allyl gives the $\Delta\delta$ value from 0.90 to 1.01 ppm for 5 examples in $CDCl_3$, and a conjugated π-allyl gives the value of 1.28 or 1.27 in three cases (Table 1). Di-μ-acetato complexes also follow this rule. The results are interpreted as follows. The electronic effect of a substituent on the central carbon of a π-allyl group delivered through the carbon-carbon bond is nearly equal for *syn* and *anti* protons of a π-allyl group, and is cancelled in the remainder of the subtraction of their chemical shifts. The $\Delta\delta$ value is, therefore, nearly constant for isolated π-allylic palladium complexes having the same anion ligands. For π-allyls adjacent to unsaturated bonds, however, magnetic anisotropy of the unsaturated carbons influences *syn* and *anti* protons unequally, and gives different $\Delta\delta$ values from those of isolated π-allyl groups. The spectra of I, in which ring formation hinders the rotation of bonds, show that the *syn* proton of a π-allyl suffers a deshielding effect by an adjacent unsaturated carbon and the *anti* proton suffers more shielding.



I : X=CH_3COO Y=H
III : X=CH_3COO Y=D
VI : X=Cl Y=H
VII : X=$CH_3COCHCOCH_3$ Y=H



II : X=CH_3COO
V : X=$CH_3COCHCOCH_3$



IV

Synthesis of Complex I from Di-μ-acetato-2,2′-bi-π-allyldipalladium and Allene. Complex I was also synthesized in a high yield by bubbling allene into a dichloromethane solution of di-μ-acetato-2,2′-bi-π-allyldipalladium (II).

$$Pd_2(C_3H_4)_2(CH_3COO)_2 + C_3H_4 \longrightarrow Pd_2(C_3H_4)_3(CH_3COO)_2$$
(II) (I)

The reaction proceeded almost quantitatively. when allene-d_4 was used for this reaction, $Pd_2(C_9H_8D_4)(CH_3COO)_2$ (III) was obtained. NMR spectra of III are shown in Fig. 2. The spectra show that two absorptions at δ 3.65 and 2.78 ppm in the corresponding complex I have disappeared. The structure of tetradeutero complex III clearly indicates that this complex is formed *via* insertion of allene between the bridged bi-π-allyl and palladium. The coupling of newly coordinated allenes with replacement of π-allyl ligands,

Table 2. Comparison of the raectivity for insertion of allene

CH_2Cl_2, 20 m*l*; complex, 0.222 mmol; allene, 100 m*l*; room temperature, 15 hr

Complex	Product (%)	
$Pd_2(C_3H_4)_2(CH_3COO)_2$ (II)	$Pd_2(C_3H_4)_3(CH_3COO)_2$	(93.5)
$Pd_2(C_3H_4)_2(CH_3COCHCOCH_3)_2$ (V)	recovered	(86.6)
$Pd_2(C_3H_5)_2(CH_3COO)_2$ (IV)	recovered	(99.9)
$Pd_2(C_3H_4)_3(CH_3COO)_2$ (I)	recovered	(87.5)

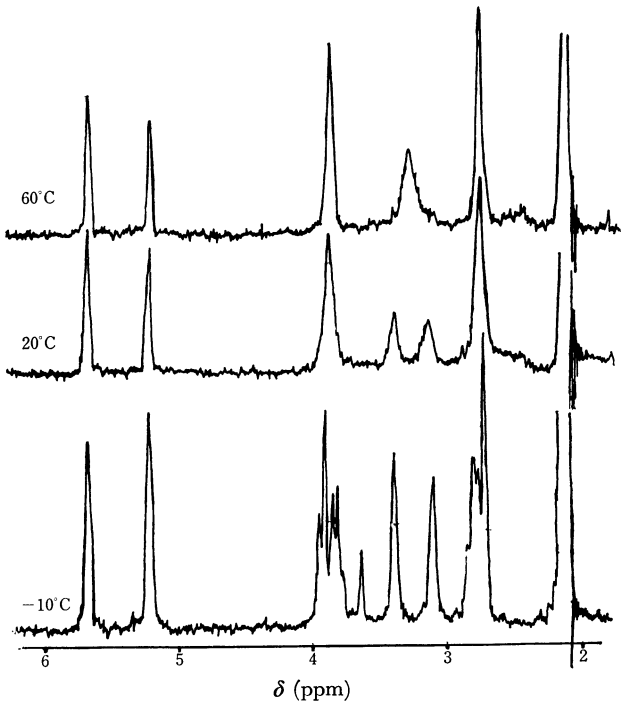


Fig. 2. Temperature-dependent NMR spectra of III (in $CDCl_3$).

observed by the reaction of allene with acetylacetonato-π-allylpalladium,[2k] did not take place in this case.

Such a bridge elongation by insertion has not yet been reported and suggests that there is some allowance in length of the ligand bridging two palladium metals combined with μ-acetato ligands. The result is interesting from the fact that palladium acetate acts as a catalyst for dimerization[7,8] or co-dimerization[9] of ethylenic compounds and arenes.

Concerning insertion, the reaction was found to be an assisted one. Experimental results are listed in Table 2. Under the same conditions as in the reaction of allene and II, di-μ-acetato-bis(π-allylpalladium) (IV) and bis(acetylacetonato)-2,2′-bi-π-allyldipalladium (V) did not insert allene, and the substrates were recovered almost quantitatively. Thus, it is clear that the acceleration observed for II is not simply due to the presence of μ-acetato ligands or a bi-π-allyl ligand. Hughes and Powell reported that there is some strain in complex II on the basis of its NMR spectra of a lower symmetry than C_{2v} and that rigid μ-acetato bridges impart the strain.[2k] Temperature-independent spectra from −100°C to 60°C suggest that no exchange of the μ-acetato ligand occurs in this complex at least faster than NMR time scale. Temperature-dependent NMR spectra of I and simple inspection of a scaled model suggest there is less strain in this complex.

The insertion of allene might be explained to occur easily by the relief of the strain in the substrate complex. This is a new factor besides steric repulsion and electronic factors[10] controlling the insertion into a π-allyl-metal bond.

Derivatives of I. When I was treated with an aqueous sodium chloride solution, it exchanged all acetate ligands for chloride ions, and a yellowish gray complex, dichloro-[2,2′-(1-methyleneethylene) bis-π-allyl]dipalladium (VI), was precipitated. Complex I was regenerated from VI by treatment with silver acetate in acetone. An acetylacetonato complex, bis-(acetylacetonato)-[2,2′-(1-methyleneethylene) bis-π-allyl]dipalladium (VII), was obtained from VI as usual with thallium acetylacetonate.[2j] The NMR spectrum of VII was similar to the spectra of I at high temperatures.

Temperature-dependent NMR Spectra of I and III. I shows temperature-dependent NMR spectra and the spectra at low temperatures are very complicated due to the overlap of absorptions. In the case of tetradeutero complex III, however, interpretation of the spectra became simple. At −10°C, two saturated methylene protons of complex III exhibited AB type couplings with a coupling constant of 15.5 Hz. This value is reasonable for the coupling constant of geminal methylene protons on a sufficiently large ring. It shows that the ring is fixed at the temperature. With the rise of temperature, the AB quartet changed into a broad doublet at room temperature, and finally coalesced

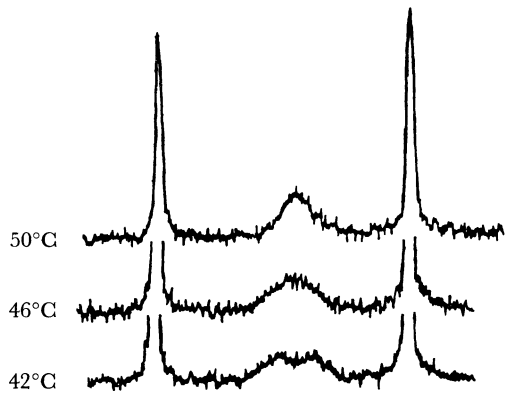


Fig. 3. Coalescence of the AB quartet of III.

7) C. F. Kohll and R. van Helden, *Rec. Trav. Chim. Pays-Bas*, **86**, 193 (1967).

8) J. M. Davidson and C. Triggs, *Chem. Ind.* (London), **1966**, 457.

9) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

10) Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **16**, 177 (1969).

into a singlet at 46°C (Fig. 3). As the origin of the dynamic nuclear magnetic resonance observed, two factors might be considered, the molecular fluctuation of the complex, and the dissociation of the μ-acetato bridge followed by the rotation of the organic ligand. A rough estimate of the activation energy from the coalescence temperature[11] with the assumption that the frequency factor is 10^{12},[12] gave 14.5 kcal/mol, which might be too large for the energy of the former mechanism.

For π-allyl parts, the spectra of I and III are also dependent on temperature (Figs. 1 and 2). At −10°C *syn* and *anti* protons of III were each separated into two doublets with coupling constants 1.0 and 1.5 Hz, respectively. The separation between the doublets was greater for *syn* protons, as can be seen from inspection of a scaled model. Coalecsence of both doublets starts almost at the same temperature as that for saturated methylene protons, suggesting that these processes occur by the same mechanism. Contrary to what has been reported for IV,[13] the magnetic unequality in I and III would arise from the difference in a stereochmical situation against the bridging 1-methyleneethylene group.

The exchange of *syn* and *anti* protons was not detected at least until 100°C in acetic acid-d_4, indicating that no terminal CH_2 rotation is present in these complexes.

Experimental

All reagents were obtained commercially and used without further purification unless otherwise stated. Melting points were determined with a Yanagimoto melting point apparatus. IR spectra were measured as KBr pellets using a Perkin-Elmer 521 spectrometer; NMR spectra, on a Varian A-60 spectrometer for dilute solutions in the specified solvents. The chemical shifts were expressed in δ value (ppm) relative to TMS used as the internal standard. The temperature of measurement was 40°C unless otherwise specified. Mass spectra were obtained with a JMS-01SG spectrometer; the molecular weight was determined with a vapor pressure osmometer of Mechrolab-301. A gas chromatograph of Yanagimoto GCG 220 type was used for both analytical and preparative purposes.

Formation of Complex I from Allene and Palladium Acetate. Into a solution of palladium acetate[14] (5.0 g) in benzene (250 m*l*) was introduced allene gas (6.7 *l*); stirring was continued overnight at ambient temperature. After addition of hexane (250 m*l*), the resulting solution was chromatographed on silica-gel (Wako-gel C200). Stepwise elution with diethyl ether and ethyl acetate afforded complex I as an ethyl acetate solution. After evaporating the solvent, recrystallization of the residue from dichloromethane-hexane gave a pure product as a yellow crystal (0.92 g, 18.3%), mp 148—150°C (dec).

Found: C, 34.63; H, 4.10%; mol wt (benzene, 37°C), 466. Calcd for $Pd_2(C_9H_{12})(CH_3COO)_2$: C, 34.58; H, 4.11%; mol wt, 451. IR: 1620(C=C), 1570(COO^-), 1468, 1410(COO^-), 1340, 1042, 1020, 945, 932, and 760 cm^{-1}. NMR(in $CDCl_3$): 5.63 (1H, $=CH_2$), 5.17 (1H, $=CH_2$), 3.82 (2H, π-allyl), 3.65 (2H, π-allyl), 3.32 and 3.09 (2H, $-CH_2-$), 2.78 (2H, π-allyl), 2.68 (2H, π-allyl), and 2.02 ppm (6H, CH_3CO).

Hydrogenolysis of I. Complex I (0.78 mmol) was dissolved in chloroform and hydrogen was fed from a gas buret after evacuation with dry-ice cooling. A rapid gas absorption ceased in 65 min with consumption of 3.55 mmol of hydrogen.[15] The products were palladium metal, acetic acid, and hydrocarbons. The hydrocarbons were found to be a mixture of three compounds by gas chromatography (VPC, PEG 6000) with a relative ratio[16] of 37:14:50 in the order of retention time. Absence of C_3 hydrocarbons was confirmed by VPC (β,β'-oxydipropionitrile, 25°C). The three hydrocarbons were separated by gas chromatography using the same column (PEG 6000). The first effluent was identified as 2,3,5-trimethylhexane by peak to peak correspondence with the standard NMR chart (API 214). The other two products were identified as 2,3,5-trimethyl-2-hexene and 2,4,5-trimethyl-2-hexene by their NMR spectra, and mass spectra of the brominated products.

2,3,5-trimethyl-2-hexene; NMR(in CCl_4): 0.85 (d, 6H), 1.60 (s, 9H), and 1.88 ppm (s, 2H). The mass spectrum for the brominated product; m/e^+ 285 $(M-1)^+$.

2,4,5-trimethyl-2-hexene; NMR(in CCl_4): 0.7—0.9 (m, 9H), 1.4—1.6 (m, 1H), 1.57 (d, 3H), 1.67 (d, 3H), 2.03 (m, 1H), and 4.92 ppm (d, 1H), The mass spectrum for the brominated product; m/e^+ 285 $(M-1)^+$.

Calculation of the theoretical amount of hydrogen based on the molecular formula and the ratio of the three hydrocarbons above gave 3.62 mmol, which is in good accordance with the experimental value.

Synthesis of I from Di-μ-acetato-2,2'-bi-π-allyl-dipalladium. Allene gas (100 m*l*) was introduced into the dichloromethane solution (20 m*l*) of complex II[2k] (0.222 mmol), and the mixture was stirred at ambient temperature overnight. When the solvent was distilled off, a yellow crystal was obtained. Recrystallization from dichloromethane-hexane afforded I (0.207 mmol, 93.5%). Under the same conditions, tetradeutero complex III was obtained using allene-d_4,[18] mp 150—152°C (dec).

Found: C, 34.57; H, 5.06%. Calcd for $Pd_2(C_9H_8D)_4(CH_3COO)_2$: C, 34.31; H, 4.87%. IR: 1570, 1410, 1340, 1040, 1020, 940, 930, and 672 cm^{-1}. NMR(in $CDCl_3$): 5.63 (s, 1H), 5.17 (s, 1H), 3.80 (s, 2H), 3.30 and 3.08 (each broad s, sum 2H), 2.68 (s, 2H), and 2.02 ppm (s, 6H); (in $CDCl_3$, −10°C): 5.60 (s), 5.15 (s), 3.85 (d, J=1.5 Hz), 3.77 (d, J=1.0 Hz), 3.43 and 2.93 (AB, J=15.5 Hz), 2.72 (d, J=1.0 Hz), 2.65 (d, J=1.5 Hz), and 2.05 ppm (s).

Comparison of Various Complexes for Insertion of Allene. Di-μ-acetato-bis(π-allylpalladium) (IV) was prepared by the method of Robinson and Shaw.[6]

Bis(acetylacetonato)-2,2'-bi-π-allyldipalladium (V) was prepared by the method of Hughes and Powell[1c] as a white crystal, mp 187—190°C (dec).

11) G. Binsch, in "Topics in Stereochemistry," Vol. 3, ed. by E. L. Eliel and N. L. Allinger, Interscience Publishers, New York, N. Y. (1968), p.97.

12) Selection of this value is arbitrary. However, from the fact that the value is in the same order as that of the interconversion of cyclohexane and the valence isomerization of bullvalene,[11] this would be a reasonable selection.

13) J. Powell, *J. Amer. Chem. Soc.*, **91**, 4311 (1969).

14) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

15) To avoid the error caused by the adsorption of hydrogen by palladium, hydrogen feeding was stopped when the rapid absorption of gas was over.

16) It was assumed that the relative response per gram of these hydrocarbons was equal. Values in literature[17] suggest that the error caused by this assumption is within 5%.

17) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

18) A. T. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1958).

Found: C, 39.06; H, 4.44%. Calcd for $Pd_2(C_6H_8)(CH_3COCHCOCH_3)_2$: C, 39.05; H, 4.50%.

The reaction conditions for insertion were the same as described above. The results are shown in Table 2.

Syntheses of Derivatives of Complex I. Dichloro-[2,2'-(1-methyleneethylene)bis-π-allyl]dipalladium (VI). To a benzene solution (20 ml) of I (0.100 g) was added an aqueous sodium chloride (0.035 g) solution (0.1 ml) and the mixture was stirred for an hour at ambient temperature. The resulting precipitate was washed with dichloromethane, acetone, and water. Recrystallization from dimethylsulfoxide-methanol gave a yellowish gray complex (0.067 g, 75%), mp 221—223°C (dec)

Found: C, 27.08; H, 3.06%. Calcd for $Pd_2C_9H_{12}Cl_2$: C, 26.76; H, 2.99%. IR: 1625, 1465, 1430, 1410, 1355, 1320, 965, 940, 850, 780, 758, 746, and 688 cm^{-1}. NMR(in DMSO-d_6): 5.73 (s, 1H), 5.37 (s, 1H), 4.38 (s, 2H), 4.18 (s, 2H), 3.23 and 3.38 ppm (m, 6H).

Complex I (0.072 g, 96%) was regenerated from VI (0.067 g) by treating with silver acetate (0.067 g) in dry acetone.

Bis(acetylacetonato)-[2,2'-(1-methyleneethylene)bis-π-allyl]dipalladium (VII). Thallium(I) acetylacetonate (0.169 g) and VI (0.112 g) were stirred in benzene (30 ml) overnight. The resulting precipitate of thallium chloride was removed by filtration, and the filtrate was evaporated to give VII. Recrystallization from dichloromethane-hexane gave a pure product as a white crystal (0.115 g, 78%), mp 150—151°C (dec).

Found: C, 42.74; H, 4.80%. Calcd for $Pd_2(C_9H_{12})(CH_3COCHCOCH_3)_2$: C, 42.94; H, 4.90%. IR: 1570, 1525, 1512, 1440, 1391, 1357, 1259, 1018, 773 cm^{-1}. NMR (in $CDCl_3$): 5.59 (s, 1H), 5.35 (d, 2H), 5.29 (m, 1H), 3.88 (s, 2H), 3.72 (s, 2H), 3.40 (s, 2H), 2.83 (s, 2H), 2.70 (s, 2H), and 1.98 ppm (s, 12H).

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