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π-Allylic Coordination of Ethyl Acetoacetate to Palladium(II)[*1]

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The ethanolysis of diketene is accelerated by the addition of sodium tetrachloropalladate(II). Yellow crystals separated in the end of this reaction were identified as di-μ-chlorobis(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) on the ground of analytical data, molecular weight and infrared spectrum. The same complex was also prepared directly by the reaction of palladium(II) chloride with ethyl acetoacetate in water.

A number of π-allylic complexes have been synthesized from palladium(II) chloride and various mono-olefins or conjugated diolefins,[1] but those of unsaturated ketones and esters have been rather few. Tsuji and Imamura[2] prepared π-allylic palladium(II) complexes from α,β- and β,γ-unsaturated esters, Parshall and Wilkinson[3] from α,β-unsaturated ketones such as mesityl oxide, and Kasahara *et al.*[4] from α,β-unsaturated cyclic ketones. This paper reports a novel type of π-allylpalladium(II) complex containing ethoxycarbonyl and hydroxy groups as substituents at 1 and 2 positions, respectively.

In a previous paper[5] we reported copper(I) chloride complex of acrolein, the structure of which has been studied by X-ray and found to contain each acrolein molecule serving as a bridging group between two copper atoms *via* the double bond and the carbonyl oxygen atom.[6] As an extention of this series an unsaturated lactone, diketene was employed as a ligand, and its reactions with several metal compounds have been studied. In the course of these studies sodium tetrachloropalladate(II) was found to catalyze the alcoholysis of diketene and deposit the plladium(II) complex of the reaction product, ethyl acetoacetate.

Experimental

Materials. Diketene supplied by Daicel, Ltd. was used immediately after distillation under reduced pressure. Commercial palladium(II) chloride was evacuated at 300°C. A mixture of palladium(II) chloride and sodium chloride in the mole ratio of 1 : 2 was dissolved in ethanol. The solvent was then evaporated up to dryness and sodium tetrachloropalladate(II) thus prepared was further dried at 100°C *in vacuo*. Dichlorobis(benzonitrile)palladium(II) was prepared by the direct reaction between palladium(II) chloride and benzonitrile according to the Kharasch's method.[7] Dichloromethane, benzene and alcohols were purified by standard methods.[8]

Measurements. Palladium was determined gravimetrically as the dimethylglyoximato complex and chlorine as the silver salt.[9] The molecular weight was determined by the method of boiling point elevation of benzene. The ultraviolet absorption spectra were measured with a Hitachi EPS-2 recording spectrophotometer, and the infrared absorption spectra by means of a Hitachi infrared spectrophotometer EPI-2 or a Shimadzu infrared spectrophotometer IR-27. The proton magnetic resonance spectra were measured with a 60 Mc spectrometer, model JNM 3H 60 of Japan Electron Optics Laboratory, Ltd.

Reaction of Sodium Tetrachloropalladate(II) with Diketene in Ethanol. To a solution of sodium tetrachloropalladate(II) (5.6×10^{-3} mol) in ethanol (70 m*l*) was added gradually an ethanol solution of diketene

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1) For example, M. L. H. Green and P. L. I. Nagy, "Advances in Organometallic Chemistry," Vol. 2, ed. by F. G. A. Stone and R. West, Academic Press, New York (1964), p. 325; R. Hüttel, *et al., Chem. Ber.*, **98**, 1753 (1965); M. S. Lupin, J. Powell and B. L. Shaw, *J. Chem. Soc.*, (*A*), **1966**, 1687.

2) J. Tsuji and S. Imamura, This Bulletin, **40**, 197 (1967).

3) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

4) A. Kasahara, K. Tanaka and K. Asamiya, This Bulletin, **40**, 351 (1967).

5) S. Kawaguchi and T. Ogura, *Inorg. Chem.*, **5**, 844 (1966).

6) Y. Kushi, T. Ogura, S. Kawaguchi and H. Kuroya, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

7) M. S. Kharasch, *J. Am. Chem. Soc.*, **60**, 882 (1938).

8) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed., Interscience, New York, (1955).

9) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2, 9th ed., Wiley, New York (1942), pp. 140, 291.

(1.18×10^{-2} mol) under stirring at room temperature. Together with white sodium chloride yellow palladium complex precipitated, which was recrystallized from benzene. The yield of light yellow needles was about 20% on the base of palladium employed.

Found: C, 26.79; H, 3.29; Cl, 12.8; Pd, 39.33%. Calcd for $C_6H_9O_3ClPd$: C, 26.56; H, 3.32; Cl, 13.1; Pd, 39.27%.

If a more dilute solution of sodium tetrachloropalladate(II) is employed, the ethanolysis of diketene is catalyzed by palladium(II), resulting in ethyl acetoacetate, but the ester complex is not separated due to its solubility. In one experiment a solution of 2.5 mg (8.5×10^{-6} mol) of sodium tetrachloropalladate(II) and 0.25 m*l* (3×10^{-3} mol) of diketene in 2 m*l* (40×10^{-3} mol) of ethanol was kept for 5 hr at 15°C. The gas chromatogram of this solution showed three peaks ascribable to diketene, ethanol and ethyl acetoacetate, and the conversion of diketene was estimated to be 90%. When a diketene solution in ethanol without the palladium(II) catalyst was kept standing overnight at room temperature, no trace of ethyl acetoacetate was found in the solution. The ethanolysis of diketene can thus be concluded not to proceed without a catalyst under these conditions.

Reaction of Palladium(II) Chloride with Ethyl Acetoacetate in Water. Palladium chloride (5.6×10^{-3} mol) was dissolved in 100 m*l* of water, to which ethyl acetoacetate (4.6×10^{-2} mol) was added. The mixture was kept at 40—60°C under stirring for about 40 hr. Brown precipitate formed was filtered off and the filtrate was kept standing for about 70 hr at room temperature. Yellow precipitate appeared, which was recrystallized from benzene, and the yield was about 20% on the base of palladium. The analytical data agree with values calculated for $PdCl(C_6H_9O_3)$ just as did the complex obtained in the reaction between sodium tetrachloropalladate(II) and diketene in ethanol.

Found: C, 26.88; H, 3.56; Cl, 13.2; Pd, 38.60%.

In a similar way the palladium(II) complex of methyl acetoacetate was prepared in the yield of about 10%. The solubilities of this complex in various solvents are even poorer than those of the complex of ethyl acetoacetate.

Found: C, 23.51; H, 3.02; Cl, 13.9; Pd, 41.00%. Calcd for $(C_5H_7O_3)PdCl$: C, 23.26; H, 3.10; Cl, 13.76; Pd, 41.25%.

Reaction of Dichlorobis(benzonitrile)palladium(II) with Diketene in Benzene. In the nitrogen atmosphere a benzene solution (500 m*l*) of dichlorobis(benzonitrile)palladium(II) (2.6×10^{-3} mol) was kept at around 60°C under stirring, to which 3.6×10^{-2} mol of diketene in 50 m*l* of benzene was added gradually. The solution turned from brown to yellow and yellow precipitate resulted. Yield of the crude product was about 80% on the base of palladium. After reprecipitation from ethanol by addition of petroleum ether the palladium complex gave the following analytical results.

Found: C, 20.71; H, 2.37; Cl, 16.02; Pd, 46.08%. Calcd for $C_4H_5O_2ClPd$: C, 21.15; H, 2.20; Cl, 15.63; Pd, 46.89%.

Reaction of Dichlorodi-μ-chlorobis(ethylene)dipalladium(II) with Diketene in Benzene. The reactant complex was prepared by the reaction between dichlorobis(benzonitrile)palladium(II) and ethylene in benzene according to the Kharasch's method.[7] A suspension of $PdCl_2(C_2H_4)$ (2×10^{-3} mol) in 250 m*l* of benzene was kept in the nitrogen atmosphere at room temperature under stirring, to which 3×10^{-2} mol of diketene in benzene was added gradually. The reaction mixture which was orange yellow at first turned to blue yellow and separated some solid. The precipitate was washed with benzene and dried at 80°C *in vacuo*. Results of the elemental analysis agreed again with values calculated for $PdCl(C_4H_5O_2)$.

Found: C, 20.43; H, 2.47; Pd, 46.07%.

Syntheses of Reference Complexes. Bis(acetylacetonato)palladium(II) was prepared by the reaction between palladium(II) chloride and excess amount of acetylacetone in water at around 60°C. Yellow complex obtained was recrystallized from benzene and dried at 100°C *in vacuo*.

Found: C, 39.57; H, 4.87%. Calcd for $(C_5H_7O_2)_2Pd$: C, 39.42; H, 4.60%.

Nickel(II) complex of ethyl acetoacetate was synthesized by the reaction between the nickel ammine complex and the ester in water. The product was recrystallized from dichloromethane and dried at 100°C *in vacuo*.

Found: C, 40.82; H, 6.27%. Calcd for $Ni(C_6H_9O_3)_2 \cdot 2H_2O$: C, 40.24; H, 6.43%.

Results and Discussion

Di-μ-chlorobis(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II). Light yellow crystals which were produced in the reaction of sodium tetrachloropalladate(II) with diketene in ethanol have the empirical formula $PdCl(C_6H_9O_3)$. When this compound was heated at around 180°C *in vacuo*, partial carbonization occurred and volatile substance was evolved, which was identified as ethyl acetoacetate by means of the gas chromatography and infrared spectra. It was also decomposed by dilute hydrochloric acid to set free ethyl acetoacetate. These results indicate that this is a palladium(II) complex of ethyl acetoacetate.

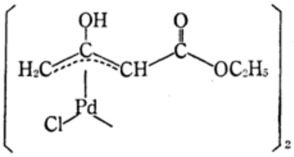
This complex is slightly soluble in benzene, dichloromethane, methyl and ethyl alcohols (10^{-2}—10^{-3} mol/*l* at room temperature). It is more soluble in dimethyl sulfoxide, but reddish yellow precipitate is separated therefrom on standing, which shows an identical infrared spectrum with what is obtained in the reaction between palladium(II) chloride and dimethyl sulfoxide. Tetrahydrofuran and pyridine also show high solubilities, but decomposition of the complex resulted on standing in either case. The molecular weight of this palladium(II) complex was determined to be 502 by measuring the boiling point elevation of benzene. This value nearly coincides with 541 calculated for the dimer, certifying the molecular formula $[PdCl(C_6H_9O_3)]_2$ and satisfying the usual coordination number four of palladium(II).

The infrared spectra were measured in the region of 400 through 5000 cm^{-1} by the potassium bromide disk method. Characteristic absorption bands are listed in Table 1 together with those for the corresponding complex of methyl acetoacetate. Infrared

TABLE 1. CHARACTERISTIC INFRARED ABSORPTION BANDS OF DI-μ-CHLOROBIS(π-1-ETHOXYCARBONYL-2-HYDROXYALLYL)DIPALLADIUM(II) (A) AND DI-μ-CHLOROBIS(π-1-METHOXYCARBONYL -2-HYDROXYALLYL)DIPALLADIUM (II) (B) DETERMINED IN THE POTASSIUM BROMIDE DISK

Compex A, cm^{-1}	Complex B, cm^{-1}	Assignment
3200 m	3160 m	O–H str.
3080 w	3080 w	end methylene str.
1675 vs	1670 vs	C=O str.
1445 s	1435 s	delocalized C–C str.
1205 vs	1220 vs	COC asym. str.
1170 s 1040 m	1170 s 1035 m	COC sym. str. delocalized C–C str. C–OH str.
545 m	545 m	skeletal deform.

spectra of ethyl acetoacetate[10] and di-μ-chlorobis-(π-allyl)dipalladium(II)[11] were referred to in assigning absorption bands of the present complex. Although bis(acetylacetonato)palladium(II) is well known to be a usual enolate chelate,[12] corresponding palladium(II) complex of ethyl acetoacetate has not yet been reported. As shown in Table 1, the present complex does not show C=O and C=C stretching bands characteristic for the enolate chelate,[13] but has very strong peaks at 1675 and 1205 cm^{-1} indicating the presence of uncoordinated ethoxycarbonyl group. The peak at 3200 cm^{-1} must be attributed to an OH group. It is a quite novel and rather curious feature that the OH group of an enol form is preserved intact in this β-dicarbonyl complex. On the other hand peaks at 3080 and 1445 cm^{-1} may be ascribed to the stretching vibrations of end methylene and π-allylic C–C bonds, respectively.[11] Furthermore the absorption band at 546 cm^{-1} might be attributable to the skeletal deformation which was assigned by Fritz[11] as characteristic for the π-allyl group. These infrared informations strongly suggest the formula I for the palladium(II) complex of ethyl acetoacetate.



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The stretching band of OH usually appears[14] at around 3600 cm^{-1}, and that of C=O at 1740 and 1715 cm^{-1} in the case of free ethyl acetoacetate. These bands are observed at 3200 and 1675 cm^{-1}, respectively in case of the present complex. These shifts to the lower frequency side suggest the presence of inter- or intramolecular hydrogen bonding between the two functional groups.

Proton magnetic resonance spectra are frequently utilized as one of the most powerful tools in the structural study of π-allylic metal complexes.[15] Unfortunately, however, suitable inert solvents are not available for the present complex. It is not enough soluble in alcohols or haloalkanes, and reacts with dimethyl sulfoxide and other better solvents. Thus useful informations can not be obtained from these studies. The X-ray analysis of this complex is now in progress and preliminary results[16] clearly support the structure I, and certify the presence of intermolecular hydrogen linkage which constitutes a one-dimensional polymeric structure. The palladium(II) complex of ethyl acetoacetate can now be named as di-μ-chloro-bis-(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II).

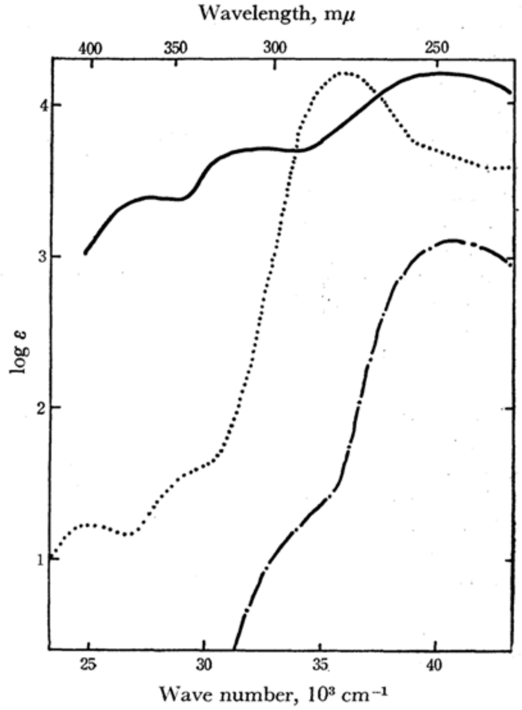

Fig. 1. Ultraviolet absorption spectra of ethyl acetoacetate ($C_6H_{10}O_3$) (–•–•), Ni($C_6H_9O_3$)$_2$ (·········) and [PdCl($C_6H_9O_3$)]$_2$ (———).

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[10] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York (1957), pp. 178.

[11] H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

[12] K. Nakamoto, P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

[13] G. T. Behnke and K. Nakamoto, *ibid.*, **6**, 433 (1967).

[14] p. 95 of Ref. 10.

[15] See, for instance, J. K. Becconsall, B. E. Job and S. O'Brien, *J. Chem. Soc.*, (*A*), **1967**, 423; W. B. Wise, D. C. Lini and K. C. Ramey, *Chem. Commun.*, **1967**, 463.

[16] K. Oda, N. Yasuoka, N. Kasai, M. Kakudo, Y. Tezuka, T. Ogura and S. Kawaguchi, *Chem. Commun.*, **1968**, 989.

The ultraviolet spectrum of this complex in ethanol is shown in Fig. 1 together with those of ethyl acetoacetate and its nickel(II) complex. A very broad band at around 250 mμ seems to be characteristic of the ligand. The nickel(II) complex of ethyl acetoacetate shows absorption maxima at 690 and 403 mμ, of which the extinction coefficients are both small and attributable to the d–d transition. The present π-allylic complex has very strong bands at 358 (log $\varepsilon=3.38$) and around 310 mμ (log $\varepsilon=3.69$). These absorptions may be related to the π-allylic structure of the complex. The absorption data of a related compound di-μ-chlorobis(π-1-methoxymethylallyl)dipalladium(II) in methanol were reported by Robinson and Shaw,[17] which show maxima at 330 (log $\varepsilon=2.98$), 229 sh (log $\varepsilon=3.86$) and 208 mμ (log $\varepsilon=4.19$). Some correspondence seems to exist between absorption data of these π-allylic palladium complexes, but their exact assignments are not possible.

Uncharacterized Complex PdCl($C_4H_5O_2$). The analytical data of the complex obtained in the reaction between dichlorobis(benzonitrile)palladium(II) and diketene nearly coincide with those calculated for PdCl($C_4H_5O_2$). It is hardly soluble in benzene or haloalkanes,but dissolves pretty well in methyl and ethyl alcohols. The same compound was also obtained in the reaction between dichloro-di-μ-chlorobis(ethylene)dipalladium(II) with diketene in benzene. The analytical and infrared data suggest that this is not a complex of diketene itself. The nature of this complex is now under investigation.

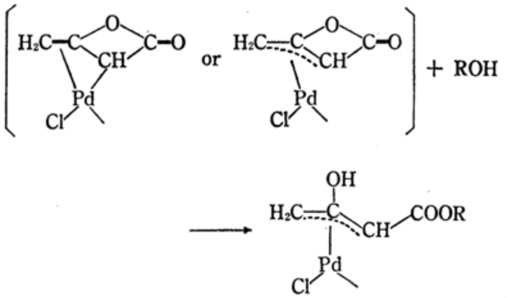
The Mechanism of Alcoholysis of Diketene in the Presence of Pd(II). When excess amount of diketene is added to an ethanol solution of sodium tetrachloropalladate(II), color of the solution turns from red to yellow in a few minutes and sodium chloride precipitates at the same time. Then irritative ordor of diketene changes gradually to agreeable one of the ester. Ethyl acetoacetate produced was identified by means of the gas chromatography.

The palladium(II) complex of the ester was deposited in the end of reaction when the tetrachloropalladate(II) was used in a higher concentration. This is a complex of the reaction product, and during the steady course of the catalytic alcoholysis of diketene, the ligand ester must be easily displaced by the substrate, diketene.

Diketene is known to be an acid of medium strength (p$K_a=7.1$),[18] and will liberate a proton to coordinate to palladium.

$$Na_2PdCl_4 + C_4H_4O_2 \rightleftarrows \underset{\text{II}}{PdCl(C_4H_3O_2)} + HCl + 2NaCl \qquad (1)$$

The intermediate II has not yet been identified but is just presumed here. The strong acidity of the reaction mixture and precipitation of sodium chloride support Eq. (1). The nucleophilic attack of an alcohol molecule on the carbonyl carbon may result in the rupture of the lactone ring.



(2)

The relative rate of the Pd(II) catalyzed alcoholysis in various aliphatic alcohols are in the decreasing order of MeOH$>$EtOH$>$ n-PrOH$\sim$$i$-PrOH. This is the same tendency as that observed for the acid catalyzed esterification. Detailed informations concerning the mechanism of Pd(II) catalyzed alcoholysis of diketene must await further investigations.

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17) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806.

18) A. Wassermann, *ibid.*, **1948**, 1323.