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Preparation and Properties of Inclusion Compounds of η^3-Allylpalladium Complexes with Cyclodextrins

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Inclusion compounds of di-μ-chloro-bis(η-allyl)dipalladium and its analogues with cyclodextrins (CDs; α-CD, β-CD, and γ-CD) were prepared. One-to-one inclusion compounds were obtained in high yields by the treatment of β- and γ-cyclodextrin with di-μ-chloro-bis(η-allyl)dipalladium and its analogues. The formation of inclusion compounds is selective. β-CD formed inclusion compounds with di-μ-chloro-bis[1-3-η-(2-methylallyl)]dipalladium in high yield, but it did not form any inclusion compounds with di-μ-chloro-bis(1-3-η-2-butenyl)dipalladium. γ-CD formed inclusion compounds with all the η^3-allylpalladium complexes tested in high yields. α-CD did not form inclusion compounds with any η^3-allylpalladium complexes tested. The thermogravimetric measurements show that η^3-allylpalladium complexes are stabilized when they are included in the CD cavity. The inclusion compounds were characterized by ^{1}H NMR, IR, UV, and circular dichroism spectra.

Organotransition metal complexes have been extensively used as homogeneous catalysts in organic reactions and much effort has been paid to improve their activity and selectivity.[1] Meanwhile, cyclodextrins (CDs) have been studied as a model of enzyme for selective catalysts. Therefore to combine the function of organometallic complexes and that of cyclodextrins, we tried to prepare the inclusion compounds of organometallic complexes with cyclodextrins. There are a large number of reports on the inclusion compounds of organic molecules with cyclodextrins.[2,3] In marked contrast, there are only a few reports on the inclusion compounds of organometallic complexes with cyclodextrins.[4,5] We previously reported the preparation and properties of inclusion compounds of ferrocene and its analogues with cyclodextrins as an example of cyclodextrin inclusion compounds of organometallic complexes.[6–9] These observations prompted us to examine the interaction of CD with η^3-allylpalladium complexes which are frequently used in a variety of organic syntheses. Moreover, recently much attention has been devoted to the preparation and properties of inclusion compounds of more than one metal center because of their importance of the cooperative effects.[10] Now we found that β- and γ-cyclodextrin form inclusion compounds with some η^3-allylpalladium complexes and that the formation of the inclusion compounds is selective. In a previous letter,[11] we reported briefly on the preparation of inclusion compounds of π-allyl palladium complexes. We describe here the preparation and properties of inclusion compounds of di-μ-chloro-bis-(η-allyl)dipalladium, [(η-allyl)PdCl]$_2$, and its analogues with cyclodextrins in detail and discuss the binding mode. These inclusion compounds are the first inclusion compounds accommodating dinuclear species in a single cavity of CD. We also found that allylpalladium complexes are stabilized when they are included in the CD cavity.

Results and Discussion

Preparation of Inclusion Compounds. Di-μ-chloro-bis(η-allyl)dipalladium, [(η-C_3H_5)PdCl]$_2$, and its analogues are almost insoluble in water. So a cocrystallization method from aqueous solutions, which is usually used to obtain inclusion compounds with water-soluble compounds, cannot be used in this case. We tried to prepare the inclusion compounds by direct addition of fine crystals of π-allylpalladium complexes into a saturated aqueous solution of cyclodextrin at 35 °C. The product precipitated was washed thoroughly with water to remove remaining CD, and dried in vacuo. Unincluded metal complexes were removed by washing with chloroform. During this process, the included guest was not liberated from the CD cavity.

The inclusion compounds are characterized by elemental analysis and their IR, UV, and ^{1}H NMR spectra. Stoichiometries were determined by elemental analysis, including atomic absorption analysis of the metal contents, and from their ^{1}H NMR and UV spectra. All the inclusion compounds obtained in this work were stoichiometric one-to-one complexes. β-CD and γ-CD formed 1 : 1 inclusion compounds even if they were treated with two molar excess of η^3-allylpalladium complexes. This result indicates that the interaction between cyclodextrin and η^3-allylpalladium complexes is a real inclusion phenomenon. Table 1 shows the results on the preparation of inclusion compounds of η^3-allylpalladium complexes with CD. β-CD and γ-CD formed 1 : 1 inclusion compounds with allylpalladium complexes, regardless of the molar ratio of the host to guest in the reaction. γ-CD formed 1 : 1 inclusion compounds with all the η^3-allylpalladium complexes tested in high yields. The inclusion compounds of [(η-allyl)PdCl]$_2$ and [(η-allyl)PdBr]$_2$ with γ-CD were obtained in quantitative yields. β-CD formed 1 : 1 inclusion compounds with

Table 1. Preparation of Inclusion Compounds of η^3-Allylpalladium Complexes with Cyclodextrins

Guest	CD : Guest	Yield[a)] %	Product Pd(%) Found	Calcd
[(η-Allyl)PdCl]$_2$	1:2	0	—	—
	1:1	21	—	—
	1:2	48	12.4	13.2
	1:1	68	—	—
	1:2	100	11.6	11.9
[1-3-η-(2-Methylallyl)PdCl]$_2$	1:2	0	—	—
	1:1	61	—	—
	1:2	95	14.8	13.0
	1:1	58	—	—
	1:2	63	9.6	11.7
[1-3-η-(2-Butenyl)PdCl]$_2$	1:2	0	—	—
	1:2	0	—	—
	1:2	96	7.6	11.7
[(η-Allyl)PdBr]$_2$	1:2	0	—	—
	1:2	23	12.7	12.5
	1:2	100	13.2	11.3
[(η-Allyl)PdI]$_2$	1:2	0	—	—
	1:2	0	—	—
	1:2	77	12.5	10.8

a) Calculated from cyclodextrin.

[1-3-η-(2-methylallyl)PdCl]$_2$ in high yield, but it did not form inclusion compounds with [(1-3-η-2-butenyl)PdCl]$_2$ complex. β-CD also formed 1 : 1 inclusion compounds with the chloro- and bromo-bridged complexes in moderate yields but not with the iodo-bridged complex. The yields of the inclusion compounds decreased in the order Cl>Br≫I. β-CD is apparently able to discriminate not only the position of the substituents on the π-allyl ligands but the size of the bridging halogens. α-CD did not form inclusion compounds with any η^3-allylpalladium complexes tested. It is reasonable because the examination of CPK models shows that these allylpalladium complexes are too large to fit in the α-CD cavity.

Properties of Inclusion Compounds. η^3-Allylpalladium complexes are stabilized thermally by the formation of the inclusion compounds with cyclodextrin. Di-μ-chloro-bis(η-allyl)-dipalladium, for example, did not decompose on heating at 170 °C in vacuo when it was included in cyclodextrin. At this temperature the unincluded η^3-allylpalladium complex decomposes to give allyl chloride and palladium metal. Figure 1 shows the results on the thermogravimetric analysis of the inclusion compounds of di-μ-chloro-bis(η-allyl)dipalladium with β-cyclodextrin under nitrogen atmosphere, together with that of the mixture of β-CD and the allylpalladium complex, and that of the free allylpalladium complex. η^3-Allylpalladium complex starts to decompose at 145 °C and shows about 42% weight loss by 190 °C. This weight loss corresponds to 2 moles of allylchloride. In the case of the inclusion compounds there is no significant change until 190 °C except for the weight loss due to the dehydration. Rapid weight loss was observed around 200 °C, probably due to the decomposition of the guest molecule (liberation of allyl ligands). In the case of the mixture the allylpalladium complex decomposes at 145 °C. The decomposition point of π-allylpalladium rose about 50 °C by the formation of inclusion compounds. This is the first observation that metal complex is stabilized by the formation of inclusion compounds with cyclodextrin. γ-CD did not show such a stabilizing effect. On the other hand the decomposition point of β-CD was lowered by the presence of palladium complexes. Uncomplexed β-CD melts and decomposes at about 300 °C, but β-CD

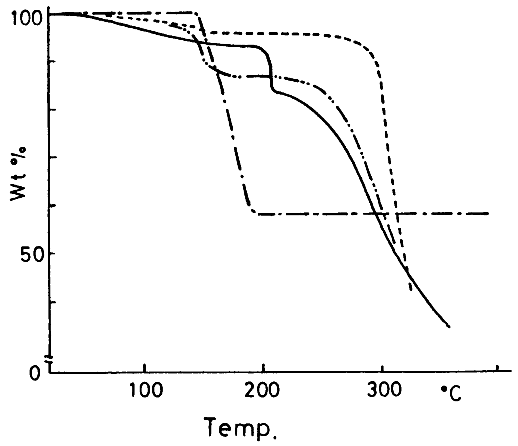

Fig. 1. Thermogravimetric analyses of the inclusion complex of [(η-allyl)PdCl]$_2$ with β-CD (——), the mixture of β-CD and [(η-allyl)PdCl]$_2$ (—·—·—), [(η-allyl)PdCl]$_2$ (—·—), and β-CD (-----) in vacuo at 5 °C min^{-1}.

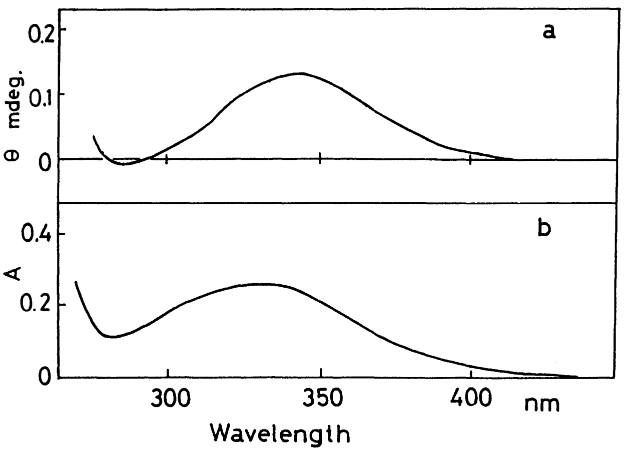

Fig. 2. Circular dichroism spectrum (a) and absorption spectrum (b) of $[(\eta\text{-allyl})PdCl]_2$ in the presence of β-CD in ethylene glycol at 25 °C. [cyclodextrin] $=[(\eta\text{-allyl})PdCl]_2=10^{-3}$ mol dm^{-3}.

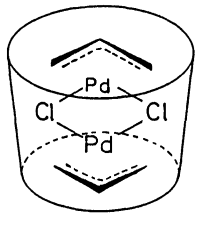

Fig. 3. Proposed structure of the inclusion compound of $[(\eta\text{-allyl})PdCl]_2$ with β-cyclodextrin.

in the inclusion compound starts to decompose around 200 °C. β-CD also decomposes around 200 °C in the presence of palladium complexes.

The inclusion compounds are insoluble in usual organic solvents such as benzene, hexane, chloroform, and so on. They are soluble in ethylene glycol, dimethyl sulfoxide, and *N,N*-dimethylformamide, and slightly soluble in water. However, the inclusion compounds have been found to dissociate in dimethyl sulfoxide or in *N,N*-dimethylformamide. The inclusion behavior was observed in ethylene glycol solution.

Figure 2 shows the absorption spectra and circular dichroism spectra of $[(\eta\text{-allyl})PdCl]_2$ in the presence of β-CD in ethylene glycol solution. β-CD causes a positive Cotton effect at about 345 nm with a small negative Cotton effect around shorter wavelength. γ-CD showed no effects. These results indicate that $[(\eta\text{-allyl})PdCl]_2$ is included in the β-CD cavity with a fixed orientation and are in accordance with those of the inclusion compounds of β-CD–ferrocene and β-CD–arene chromium complexes, which show both positive Cotton effects in the longer wavelength region. This result indicates that π-allylpalldium complexes are included in β-CD cavity with a "perpendicular" manner as shown in Fig. 3 in a similar fashion to those of the ferrocene complex and arene chromium complexes.[7]

According to CPK molecular models, chloro-bridged allylpalladium complexes appear to fit well into the β-CD cavity, whereas bromo-bridged and iodo-bridged complexes are too large to fit in the β-CD cavity. 2-Methyl derivative is symmetric and more compact than 1-methyl derivative. So 2-methyl derivative fits well in the β-CD cavity, but 1-methyl derivative is not able to fit the cavity. Proposed structure for the β-CD-di-μ-chloro-bis(η-allyl)dipalladium is shown in Fig. 3, which could account for the selective inclusion in terms of the steric factor of both the allylic ligands and bridging halogens.

Another feature of these inclusion compounds is their stoichiometry. The inclusion compounds of di-μ-chloro-bis(cyclooctadiene)dirhodium(I) with β-cyclodextrin, which have a similar molecular structure to π-allylpalladium chloride, show 2 : 1 (CD : guest) stoichiometry,[12] whereas the inclusion compounds of π-allylpalladium complexes show 1 : 1 stoichiometry. This result can be interpreted in terms of the bulkiness of the ligands of the metal complexes. Cyclooctadienyl ligand is large enough to fill a single β-CD cavity, whereas π-allyl ligands are too small to fill the cavity which can accommodate the whole molecule of the complex resulting in one to one inclusion compounds. Consequently, the inclusion compounds contain two palladium metals in a single cavity. These inclusion compounds are the first example of those accommodating dinuclear species in a single cyclodextrin ring.

Experimental

All the manipulations were performed under an atmosphere of nitrogen.

Materials. Cyclodextrins (α-CD, β-CD, and γ-CD) were obtained from Hayashibara Biochemical Laboratories Inc. Their purities were checked by elemental analysis and optical rotation. η^3-Allylpalladium complexes were prepared according to the methods described in the literature.[13]

The inclusion compound of di-μ-chloro-bis(η-allyl)dipalladium with β-CD was prepared by adding finely ground crystals of di-μ-chloro-bis(η-allyl)dipalladium complex (0.344 g, 0.95 mmol) to an aqueous solution of β-CD ($10H_2O$ adduct, 0.658 g, 0.50 mmol) at 35 °C with stirring. The product was washed with water to remove remaining CD,

Table 2. Analytical Data of Inclusion Compounds

	Product			
	Found (%)		Calcd (%)	
	C	H	C	H
β-CD-$[(\eta\text{-allyl})PdCl]_2$	35.91	5.47	35.83	5.76
γ-CD-$[(\eta\text{-allyl})PdCl]_2$	36.03	5.67	36.25	5.85
β-CD-$[1\text{-}3\text{-}\eta\text{-}(2\text{-methylallyl})PdCl]_2$	36.43	5.90	36.68	5.91
γ-CD-$[1\text{-}3\text{-}\eta\text{-}(2\text{-methylallyl})PdCl]_2$	37.27	5.76	37.01	5.99
γ-CD-$[1\text{-}3\text{-}\eta\text{-}(2\text{-butenyl})PdCl]_2$	36.75	5.44	37.01	5.99
β-CD-$[(\eta\text{-allyl})PdBr]_2$	35.68	5.28	36.26	5.07
γ-CD-$[(\eta\text{-allyl})PdBr]_2$	34.81	5.42	34.53	5.58
γ-CD-$[(\eta\text{-allyl})PdI]_2$	33.28	5.00	32.89	5.31

and dried in vacuum. Nonincluded (η^3-allyl)palladium complex was removed by washing the residue with chloroform. The product was recrystallized from water or aqueous ethanol to give pale yellow crystals. For β-CD ($10H_2O$-dichlorobis(allyl)dipalladium complex: mp 200—205 °C (decomp).

The other inclusion compounds were prepared in a similar way and their analytical data are summarized in Table 2.

Instrumentation. Infrared spectra were taken on a Hitachi 295 spectrometer and UV spectra were recorded on a Shimadzu UV-202 spectrophotometer. ^{1}H NMR spectra were run on a JEOL FX100 spectrometer. Circular dichroism spectra were recorded on a JASCO J-205 spectropolarimeter. Thermogravimetric analysis was made using a Shimadzu thermal analyzer DT-30. Atomic absorption analysis was made using a Shimadzu A-610S atomic absorption/flame spectrophotometer.

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