CHEMISTRY LETTERS, pp. 1893-1894, 1986.

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

Akira HARADA, Mizutomo TAKEUCHI, and Shigetoshi TAKAHASHI*
The Institute of Scientific and Industrial Research,
Osaka University, Ibaraki, Osaka 567

One-to-one inclusion compounds were obtained in high yields by the treatment of β- and γ-cyclodextrins(CD) with di-μ-chloro-bis(η^3-allyl)dipalladium complex and its analogues. The formation of inclusion compounds is selective.

There are a large number of reports on the inclusion compounds of organic molecules with cyclodextrins.[1] In marked contrast, there are only a few reports on the inclusion compounds of organometallic complexes with cyclodextrins.[2] 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.[3] 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. Now we found that β- and γ-cyclodextrins form inclusion compounds with some η^3-allylpalladium complexes and that the formation of the inclusion compounds is selective. We report here the preparation and characterization of inclusion compounds of di-μ-chloro-bis(η^3-allyl)dipalladium complex $[(\eta^3\text{-allyl})PdCl]_2$ and its analogues with cyclodextrins.

Inclusion compounds of η^3-allylpalladium complexes were prepared by adding fine crystals of complexes to an aqueous solution of cyclodextrin at 40 °C with stirring. The product was washed with water to remove remaining CD, and dried in vacuum. Unincluded metal complexes were removed by washing with chloroform. During this process, the included guest was not liberated from the CD cavity.

Table 1 shows the results on the preparation of inclusion compounds of CD-allylpalladium complexes. γ-CD formed 1:1 inclusion compounds with all the η^3-allylpalladium complexes tested in high yields. The inclusion compounds of $[(\eta^3\text{-allyl})PdCl]_2$ and $[(\eta^3\text{-allyl})PdBr]_2$ with γ-CD were obtained in quantitative yields. β-CD formed a 1:1 inclusion compound with $[(2\text{-methyl-}\eta^3\text{-allyl})PdCl]_2$ in high yield, but it did not form any inclusion compound with $[(1\text{-methyl-}\eta^3\text{-allyl})PdCl]_2$ complex. β-CD also formed 1:1 inclusion compounds with chloro- and bromo-bridged complexes in moderate yields but not with iodo-bridged complex. β-CD is apparently able to discriminate not only the position of the substituents on the 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.

Table 1. Preparation of inclusion compounds of η^3-allylpalladium complexes

Guest	CD	Yield	Product		
		%	Pd %		CD:guest
			Found	Calcd	
$[(\eta^3\text{-}C_3H_5)PdCl]_2$	α	0	-	-	-
	β	48	12.4	13.2	1:1
	γ	100	11.6	11.9	1:1
$[(2\text{-Me-}\eta^3\text{-}C_3H_4)PdCl]_2$	α	0	-	-	-
	β	95	14.8	13.0	1:1
	γ	63	9.6	11.7	1:1
$[(1\text{-Me-}\eta^3\text{-}C_3H_4)PdCl]_2$	α	0	-	-	-
	β	0	-	-	-
	γ	96	9.2	11.7	1:1
$[(\eta^3\text{-}C_3H_5)PdBr]_2$	α	0	-	-	-
	β	23	12.7	12.5	1:1
	γ	100	13.2	11.3	1:1
$[(\eta^3\text{-}C_3H_5)PdI]_2$	α	0	-	-	-
	β	0	-	-	-
	γ	77	12.5	10.8	1:1

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, which are the first inclusion compounds accommodating dinuclear species in a cavity of CD.

η^3-Allylpalladium complexes are stabilized when they are included in the CD cavity. Thermogravimetric analysis shows that unincluded $[(\eta^3\text{-allyl})PdCl]_2$ decomposes at 150 °C, while it decomposes at 200 °C when included in the β-CD cavity.

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. Proposed structure for the β-CD-di-μ-chlorobis(η^3-allyl)dipalladium complex is shown in Fig. 1, which could account for the selective inclusion in terms of the steric factor of both the allylic ligands and bridging halogens.

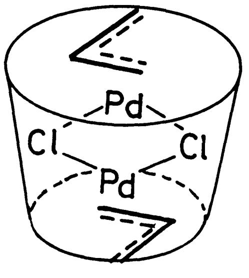

Fig. 1. Proposed structure of β-CD—$[(\eta^3\text{-}C_3H_5)PdCl]_2$.

References
1) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, Berlin (1978).
2) D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, Angew. Chem., 97, 771 (1985).
3) A. Harada and S. Takahashi, J. Chem. Soc., Chem. Commun., 1984, 645; A. Harada, K. Saeki, and S. Takahashi, Chem. Lett., 1985, 1157.

(Received August 25, 1986)