Preparation and Properties of Inclusion Compounds of (η6-Arene)tricarbonylchromium(0) Complexes with Cyclodextrins

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Inclusion compounds of η^6-arene transition-metal complexes with cyclodextrins (CDs; β-CD, γ-CD) have been prepared. One-to-one inclusion compounds were obtained in high yields in a crystalline state by the treatment of β- and γ-cyclodextrin with (η^6-arene)chromium tricarbonyl complexes. The formation of the inclusion compounds is selective. β-CD forms 1:1 inclusion compounds with (benzene)-, (toluene)-, and (o-xylene)chromium tricarbonyls but not with (mesitylene)- or (hexamethylbenzene)chromium tricarbonyls. γ-CD forms 1:1 inclusion compounds with all the (arene)chromium complexes tested. α-CD does not form inclusion compounds with any (arene)chromium tricarbonyl complexes. These inclusion compounds are thermally stable and do not liberate the guests on heating 200 °C in vacuo. The inclusion compounds were characterized by ^{1}H NMR, IR, and circular dichroism spectra.

Introduction

Recently the importance of second-sphere coordination, noncovalent coordinating influence, to transition metal complexes has been recognized, and much attention has been directed toward the field of supramolecular chemistry.[1] Inclusion compounds of transition-metal complexes with crown ethers[2] and cryptands[3] have been reported and found to have unique structures and properties. However, in these cases, their guest complexes have been limited to the complexes with protic ligands such as the amine, water, or acetonitrile ligand in the first coordination sphere. There have been few reports on the inclusion compounds with neutral transition-metal complexes without protic ligands, such as metallocenes and π-arene complexes. Such coordination modes may be possible when the host molecules have the hydrophobic cavity to accommodate these lipophilic ligands. One of the most promising candidates for such a host is cyclodextrin.

Cyclodextrins (CDs) that are naturally occurring cyclic molecules consisting of six to eight glucose units are known to form inclusion compounds with various compounds including neutral molecules.[4] Nevertheless, there are few

Table I. Preparation of Inclusion Compounds of (Arene)tricarbonylchromatin Complexes with Cyclodextrins[a]

guest arene in (η^6-arene)Cr(CO)$_3$	yield, %	
	β-CD	γ-CD
benzene	91	21
toluene	87	90
o-xylene	56	96
m-xylene	~0	84
p-xylene	~0	81
mesitylene	0	61
hexamethylbenzene	0	98
o-toluidine	45	90
o-methoxytoluene	57	98
m-methoxytoluene	3	82
guaiacol	0	52
methyl anthranilate	0	37
phenylethyl alcohol	79	100
phenylethyl acetate	61	90

[a] All the inclusion compounds are 1:1. α-CD did not give any inclusion compounds.

reports on the inclusion compounds with transition-metal complexes with cyclodextrins, although there are some reports on the interactions of organometallic complexes with cyclodextrins.[5]

In previous papers we reported the preparation and properties of cyclodextrin–ferrocene inclusion compounds as an example of cyclodextrin inclusion compounds of organotransition-metal complexes.[6] We have found that β- and γ-cyclodextrins form inclusion compounds with (η^6-arene)tricarbonylchromium(0) complexes and that the formation of inclusion compounds is selective. Previously, we reported briefly on the preparation of the inclusion

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compounds of (η^6-arene)chromium complexes with cyclodextrins.[7] We describe here the preparation and properties of inclusion compounds of (η^6-arene)tricarbonylchromium complexes with cyclodextrins in detail and discuss the selectivity and the binding mode.

Results and Discussion

Preparation of Inclusion Compounds. Since (η^6-arene)tricarbonylchromium(0) complexes are insoluble in water, the cocrystallization method from aqueous solutions, which is usually employed with water-soluble compounds to obtain inclusion complexes, cannot be used in this case. In an attempt to prepare inclusion compounds of (arene)metal complexes we tried several methods and finally found that the following method is the best.

A 2-fold molar excess of (η^6-arene)tricarbonylchromium(0) complexes was added to a saturated aqueous solution of cyclodextrin at 60 °C with stirring. The product was washed with water to remove any remaining cyclodextrin and dried in vacuo. Nonincluded (arene)tricarbonylchromium complexes were removed by washing the residue with benzene. During this process, the included guest was not liberated from the cyclodextrin cavity. The inclusion compounds were recrystallized from water and were characterized by elemental analyses and their IR and ^{1}H NMR spectra. Stoichiometries were determined by elemental analyses and the ^{1}H NMR spectra and especially the chromium contents measured by atomic absorption analyses.

Table I shows results on the preparation of inclusion compounds of CD–(η^6-arene)tricarbonylchromium(0) complexes. β-CD formed inclusion compounds with tricarbonylchromium complexes of benzene, toluene, and o-xylene in high yields and with those of m- and p-xylene in trace amounts. However, β-CD did not form inclusion compounds with mesitylene and hexamethylbenzene complexes. γ-CD formed an inclusion compound with (benzene)tricarbonylchromium in 21% yield and with all other (arene)tricarbonyl chromium complexes tested in high yields. The inclusion compound of the γ-CD–tricarbonyl(hexamethylbenzene)chromium complex was obtained almost quantitatively. It should be noted that the (benzene)tricarbonylchromium complex was selectively included in β-CD, while tricarbonylchromium complexes of mesitylene and hexamethylbenzene were specifically included in γ-CD. Of the tricarbonylchromium complexes of o-, m-, and p-xylenes, only tricarbonyl(o-xylene)chromium was selectively included in β-CD. β-CD does not show such selectivity with uncomplexed o-, m-, and p-xylenes.[8] α-CD did not form inclusion compounds with any (η^6-arene)tricarbonylchromium complexes tested, although it formed inclusion compounds with uncomplexed benzene, toluene, and xylenes.[9]

All the inclusion compounds obtained here were stoichiometric 1:1 (host to guest) complexes, even when cyclodextrin was treated with a 2-fold molar excess of (arene)tricarbonylchromium complexes.

Properties of the Inclusion Compounds. The inclusion compounds obtained are thermally stable. The inclusion compound of β-CD with (benene)tricarbonylchromium complex, for example, did not liberate the guest when heated at 150 °C under vacuum, while the nonincluded (benzene)tricarbonylchromium complex sublimed
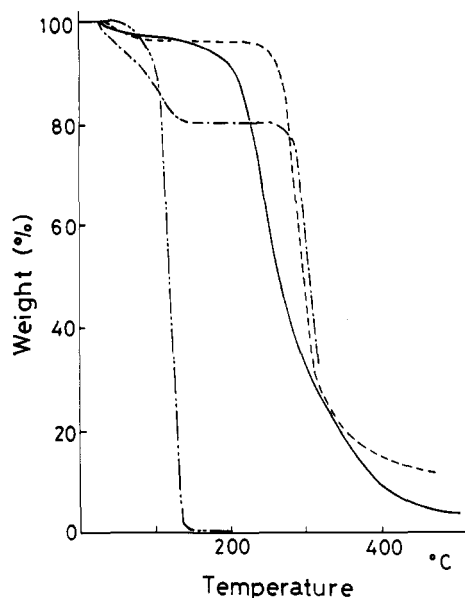

Figure 1. Thermogravimetric analysis of the inclusion compound of (η^6-benzene)tricarbonylchromium with β-cyclodextrin (—), free (η^6-benzene)tricarbonylchromium (–··–), free β-cyclodextrin (---), and the mixture of β-cyclodextrin and (η^6-benzene)tricarbonylchromium (–·–).

under the same conditions. Figure 1 shows the results of the thermogravimetric analysis of the inclusion compound of (benzene)tricarbonylchromium complex with β-cyclodextrin, free (benzene)chromium complex, free β-cyclodextrin, and a mixture of β-cyclodextrin and (benzene)chromium complex. In the case of the mixture each component behaved independently, that is, (benzene)chromium complex sublimed below 150 °C and β-cyclodextrin melts and decomposed around 300 °C. In the case of the inclusion compound there was no change around 150 °C except the loss of hydrated water. It was stable up to 200 °C and decomposed above 200 °C. These results indicate that the chromium complex is included tightly in the β-cyclodextrin cavity. The decomposing point of the inclusion compound is lower than that of cyclodextrin. This may be due to the promoting effects of chromium on the decomposition of β-cyclodextrin.

The inclusion compound of the (benzene)tricarbonylchromium complex with β-CD was stable even if it was exposed to sunlight for a prolonged period of time while that with γ-CD was unstable. The IR spectra of the inclusion compound of γ-CD showed a loss of a carbonyl ligand after irradiation with visible light for several days while the spectrum of β-CD complex did not change under the same conditions. These results indicate that β-CD binds the complex stronger than γ-CD and stabilizes the complex.

Figure 2 shows the UV and circular dichroism spectra of the (benzene)tricarbonylchromium complex in the presence of β-cyclodextrin measured in dimethylformamide solution. A positive-induced Cotton effect was observed at about 317 nm in the presence of β-cyclodextrin. This result is in accordance with that on the β-CD-ferrocene inclusion compounds,[10] indicating axial inclusion. Proposed structures for the β-CD–(η^6-benzene)tricarbonylchromium complex and the γ-CD–tricarbonyl (η^6-hexamethylbenzene)chromium complex are shown in Figure 3.

The selectivity of β-cyclodextrin for the (xylene)chromium complexes mentioned above may be interpreted on

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Table II. Analytical Data of Inclusion Compounds[a]

inclusion compound		C	H	N	Cr
β-CD-(benzene)Cr(CO)₃·H₂O	C₅₁H₇₈O₃₉Cr	44.80 (44.80)	5.95 (5.75)		3.7 (3.9)
γ-CD-(benzene)Cr(CO)₃·2H₂O	C₅₇H₉₀O₄₅Cr	44.27 (44.24)	6.16 (5.86)		3.5 (3.4)
β-CD-(toluene)Cr(CO)₃·H₂O	C₅₂H₈₀O₃₉Cr	45.02 (45.22)	5.81 (5.83)		4.3 (3.8)
γ-CD-(toluene)Cr(CO)₃·H₂O	C₅₈H₉₀O₄₄Cr	45.02 (45.13)	6.14 (5.89)		3.7 (3.4)
β-CD-(o-xylene)Cr(CO)₃·2H₂O	C₅₃H₈₄O₄₀Cr	44.88 (45.04)	6.18 (5.99)		3.8 (3.8)
γ-CD-(o-xylene)Cr(CO)₃·H₂O	C₅₉H₉₂O₄₄Cr	45.38 (45.50)	5.78 (5.95)		3.8 (3.4)
β-CD-(m-xylene)Cr(CO)₃·H₂O	C₅₃H₈₄O₄₀Cr	44.63 (45.04)	6.47 (5.99)		3.7 (3.8)
γ-CD-(m-xylene)Cr(CO)₃	C₅₉H₉₀O₄₃Cr	46.11 (46.03)	5.87 (5.87)		4.2 (3.4)
β-CD-(p-xylene)Cr(CO)₃·2H₂O	C₅₃H₈₄O₄₀Cr	44.78 (45.04)	6.14 (5.99)		3.9 (3.8)
γ-CD-(p-xylene)Cr(CO)₃·H₂O	C₅₉H₉₂O₄₄Cr	45.30 (45.50)	6.04 (5.95)		3.7 (3.4)
γ-CD-(mesitylene)Cr(CO)₃	C₆₀H₉₂O₄₃Cr	46.14 (46.39)	6.06 (5.96)		3.7 (3.3)
γ-CD-(hexamethylbenzene)Cr(CO)₃·H₂O	C₆₃H₁₀₀O₄₄Cr	46.66 (46.89)	6.41 (6.24)		3.1 (3.3)
γ-CD-(methyl benzoate)Cr(CO)₃·2H₂O	C₅₉H₉₂O₄₇Cr	44.04 (44.14)	6.16 (5.77)		3.4 (3.5)
β-CD-(o-methoxytoluene)Cr(CO)₃·2H₂O	C₅₃H₈₄O₄₀Cr	44.35 (44.54)	5.95 (5.92)		3.7 (3.7)
γ-CD-(o-methoxytoluene)Cr(CO)₃·3H₂O	C₅₉H₉₆O₄₇Cr	44.15 (44.03)	6.32 (6.01)		3.7 (3.3)
β-CD-(m-methoxytoluene)Cr(CO)₃·H₂O	C₅₃H₈₂O₄₁Cr	45.07 (45.10)	6.08 (5.85)		3.4 (3.3)
γ-CD-(m-methoxytoluene)Cr(CO)₃·2H₂O	C₅₉H₉₄O₄₆Cr	44.40 (44.43)	5.91 (5.95)		3.5 (3.3)
β-CD-(o-toluidine)Cr(CO)₃·3H₂O	C₅₂H₈₅O₄₁NCr	43.75 (43.60)	5.73 (5.98)	1.04 (0.97)	3.8 (3.8)
γ-CD-(o-toluidine)Cr(CO)₃·H₂O	C₅₈H₉₁O₄₄NCr	44.63 (44.70)	6.06 (5.88)	1.02 (0.89)	3.6 (3.4)
β-CD-(phenylethyl alcohol)Cr(CO)₃	C₅₃H₈₃O₃₉Cr	45.69 (45.69)	6.13 (5.78)		3.6 (3.7)
γ-CD-(phenylethyl alcohol)Cr(CO)₃	C₅₉H₉₀O₄₄Cr	45.73 (45.57)	5.95 (5.88)		3.4 (3.3)
β-CD-(o-methoxyphenol)Cr(CO)₃·3H₂O	C₅₂H₇₈O₄₀Cr	44.49 (44.76)	5.90 (5.63)		3.5 (3.3)
γ-CD-(methyl anthranilate)Cr(CO)₃·3H₂O	C₅₉H₉₅O₄₈NCr	43.20 (43.25)	5.90 (5.84)	0.72 (0.85)	3.0 (3.3)

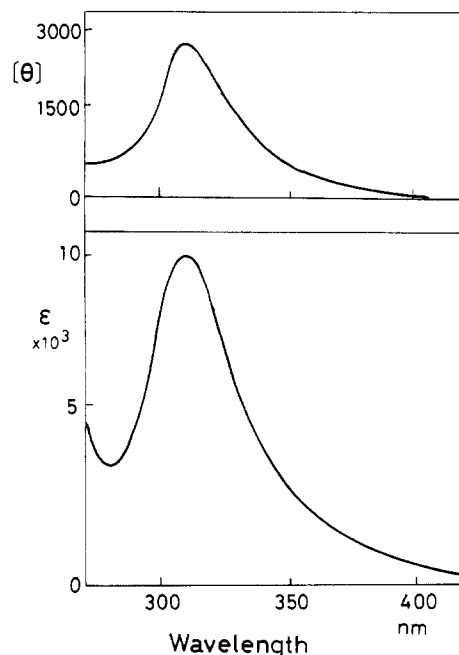[a] Required values are given in parentheses.

Figure 2. Absorption and circular dichroism spectra of (η^6-benzene)tricarbonylchromium (10^{-4} M) in the presence of β-cyclodextrin (10^{-3} M) in ethylene glycol.

Figure 3. Proposed structures of the inclusion compounds of (η^6-benzene)carbonylchromium with β-cyclodextrin (a) and that of (η^6-hexamethylbenzene)tricarbonylchromium) with γ-cyclodextrin (b).

the basis of the proposed structure of axial inclusion because β-cyclodextrin includes metal-free xylenes in an equatorial fashion and shows no selectivities to recognize the structural isomers of xylenes.

The IR spectra of the inclusion compounds show that the carbonyl streching absorptions are sharp. These spectra are different from those of the complexes in the solid, which show broad bands probably due to intermolecular interactions, and are similar to those of the complexes in solution. These results indicate that the guest complexes are isolated from each other in the cavity as in the solution.

Judging from the molecular dimensions of α-CD and (arene)tricarbonylchromium complexes, (arene)tricarbonylchromium complexes are too large to be in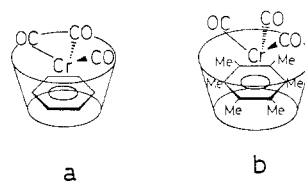cluded in the α-CD cavity. Uncomplexed benzene, toluene, and xylenes can be included in the α-CD cavity axially,[9] but a chromium tricarbonyl group hinders inclusion of the whole guest molecule because the tricarbonyl chromium group is larger than the α-CD cavity. Actually cyclodextrins do not form inclusion compounds with chromium hexacarbonyl. However, α-CD forms an inclusion complex with (η^5-cyclopentadienyl)tricarbonylmanganese to give 2:1 α-CD:guest in a high yield. This is due to the fact that α-CD is able to fit the cyclopentadienyl ring. The cyclopentadienyl ring can penetrate into α-CD as we have shown that α-CD forms inclusion complexes with the ferrocene molecule with 2:1 (CD:guest) stoichiometry.

According to CPK molecular models, tricarbonylchromium complexes of benzene and toluene appear to fit well into the β-CD cavity with axial orientation, as shown in Figure 3, whereas tricarbonylchromium complexes of mesitylene and hexamethylbenzene are too large to be included in the β-CD cavity. The γ-CD cavity is large enough to accommodate tricarbonylchromium complexes of xylene, mesitylene, and hexamethylbenzene but is too large for the (benzene)tricarbonylchromium complex. The o-xylene complex, which is more compact than the m- or p-xylene complex, fits well into the β-CD cavity.

In conclusion, β-cyclodextrin and γ-cyclodextrin form stoichiometric 1:1 inclusion compounds with (η^6-arene)tricarbonylchromium complexes efficiently and selectively, and the chromium complexes are stabilized by inclusion into the cavities of cyclodextrins.

Experimental Section

All reactions were carried out under a nitrogen atmosphere.

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. (Arene)tricarbonylchromium complexes were prepared according to the methods described in the literature.[11] Since chromium hexacarbonyl readily sublimes, spiral stainless wire was attached to the motor in the condenser to scratch the chromium carbonyl deposited back to the reaction mixture.

Preparation of Inclusion Compounds. The β-CD–(benzene)tricarbonylchromium inclusion compound was prepared by adding finely ground crystals of (benzene)tricarbonylchromium complex (0.108 g, 0.5 mmol) to an aqueous solution of β-CD (10H$_2$O adduct, 0.328 g, 0.25 mmol) at 60 °C with stirring. The product was washed with water to remove any remaining CD and dried in vacuo. Nonincluded (benzene)tricarbonylchromium was removed by washing the residue with benzene. The product was recrystallized from water or aqueous alcohol to give pale yellow crystals. β-Cyclodextrin–(benzene)Cr(CO)$_3$·7H$_2$O: mp 235–245 °C dec; IR (Nujol mull) $\nu_{C\equiv O}$ 1960, 1895 cm^{-1}; ^{1}H NMR (DMSO-d_6, 100 MHz) δ 5.68 (s, 6 H). Anal. Calcd for C$_{51}$H$_{92}$O$_{46}$Cr: C, 41.52; H, 6.14. Found: C, 40.97; H, 5.73.

The other inclusion compounds were prepared in a similar way, and their analytical and spectral data are summarized in Tables II and III.

Instrumentation. Infrared spectra were recorded on a Hitachi 295 spectrometer and UV spectra on a Shimadzu UV-202 spectrophotometer. ^{1}H NMR spectra were run on a JEOL FX100 spectrometer. Circular dichroism spectra were recorded on a

Table III. Spectral Data of Inclusion Compounds

CD	arene	IR $\nu_{C\equiv O}$ (cm^{-1})	^{1}H NMR δ, ppm (guest)
β	benzene	1895, 1960	5.5–5.8 (6 H, aromatic)
γ	benzene	1830, 1980	5.6–5.8 (6 H, aromatic)
β	toluene	1900, 1980	2.14 (3 H, methyl), 5.3–5.9 (5 H, aromatic)
γ	toluene	1890, 1975	2.14 (3 H, methyl), 5.4–5.9 (5 H, aromatic)
β	o-xylene	1880, 1970	2.14 (6 H, methyl), 5.5–5.8 (4 H, aromatic)
γ	o-xylene	1900, 1950	2.14 (6 H, methyl), 5.6–5.8 (4 H, aromatic)
β	m-xylene	1895, 1970	2.15 (6 H, methyl), 5.3–6.0 (4 H, aromatic)
γ	m-xylene	1900, 1975	2.15 (6 H, methyl), 5.3–6.0 (4 H, aromatic)
β	p-xylene	1900, 1975	2.07 (6 H, methyl), 5.3–5.9 (4 H, aromatic)
γ	p-xylene	1880, 1975	2.08 (6 H, methyl), 5.6–5.8 (4 H, aromatic)
γ	mesitylene	1875, 1950	2.15 (9 H, methyl), 5.33 (3 H, aromatic)
γ	hexamethylbenzene	1870, 1950	2.20 (18 H, methyl)
γ	methyl benzoate	1900, 1985, 1735	3.84 (3 H, methyl), 5.5–6.2 (5 H, aromatic)

JASCO J-205 spectropolarimeter. Thermogravimetric analysis was made by using a Shimadzu DT-30 thermal analyzer. Atomic absorption analysis was made by using a Shimadzu A-610S atomic absorption/flame spectrophotometer.

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# Thermochemistry of Borabenzene and Borepin

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Aspects of the thermochemistry of borabenzene and borepin are studied by means of homodesmic reactions and ab initio 6-31G* SCF energies. Model compounds for these analyses include divinylborane, 3-boraheptatriene, and the pentadienyl and heptatrienyl cations.

I. Introduction

Although the $4n + 2$ rule is successful in rationalizing the thermodynamic stability of monocyclic π systems,[1] borabenzene and borepin, two relatively simple systems with $n = 1$, still await synthesis. Borabenzene (I) does exist, however, in the form of metal complexes,[2] a pyridine adduct[3] (II, the analogue of biphenyl), the 1-phenylborabenzene anion,[4] and a dinitrogen complex of borabenzene observed at low temperature and presumed to be structure III.[5] Borabenzene adducts whose ligands are attached to boron are probably aromatic.[6]
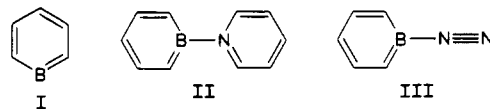
In the case of borepin (IV), which is isoelectronic with tropylium cation (V), the syntheses of 1-methylborepin[7] and 1-methyl-4,5-cyclopentenoborepin[8] have been reported recently; many aryl and benzoborepins have been known for some time.[9] Ab initio studies show borepin to be

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