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Preparation and Properties of Inclusion Compounds of Transition-Metal Complexes of Cycloocta-1,5-diene and Norbornadiene with Cyclodextrins

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Inclusion compounds of rhodium and platinum complexes of cycloocta-1,5-diene (COD) and norbornadiene (NBD) with cyclodextrins were prepared. Two-to-one (cyclodextrin to guest) inclusion compounds were obtained in high yields in a crystalline state by the treatment of β-cyclodextrin (β-CD) with bis(μ-halo)bis(η^4-cycloocta-1,5-diene)dirhodium, $[Rh(\mu\text{-}X)(COD)]_2$ (X = Cl, Br, I), and bis(μ-chloro)bis(η^4-norbornadiene)dirhodium, $[Rh(\mu\text{-}Cl)(NBD)]_2$. The formation of inclusion compounds is selective. One-to-one inclusion compounds were obtained by the reaction of β-CD with (cycloocta-1,5-diene)platinum dihalides, $Pt(COD)X_2$ (X = Cl, Br, I), in high yields, while γ-CD formed 1:1 inclusion compounds with $Pt(COD)I_2$ but not with $Pt(COD)Cl_2$. α-Cyclodextrin did not form inclusion compounds with any transition-metal complexes of cyclooctadiene and norbornadiene. The inclusion compounds are thermally stable and do not liberate the guest when heated to 200 °C in vacuo at which temperature the nonincluded guest $[Rh(\mu\text{-}Cl)(COD)]_2$ already decomposed. The inclusion compounds were characterized by ^1H NMR, IR, UV, and circular dichroism spectra. A large induced Cotton effect was observed with β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$. The ^1H NMR spectrum of $[Rh(\mu\text{-}Cl)(COD)]_2$ in the presence of β-CD shows two sets of resonances for two different CD species that are assigned to free β-CD and the complexed β-CD, respectively. The binding mode will be discussed.

Introduction

Recently the importance of molecular recognition by the formation of inclusion complexes has been recognized not only in the field of organic chemistry but also in the field of organometallic chemistry. Inclusion compounds of transition-metal complexes with crown ethers[1] and cryptands[2] have been reported and found to have unique structures and properties. However, in these cases, their guest complexes are limited to the complexes with protic ligands (NH_3, H_2O, CH_3CN) in the first coordination sphere and only part of the ligands can interact with the hosts. There have been few reports on inclusion compounds with neutral transition-metal complexes without protic ligands. Such coordination modes may be possible when the host molecules have three-dimensional hydrophobic cavities to accommodate these lipophilic ligands. One of the most promising candidates for such a host is cyclodextrin.

Cyclodextrins (CDs) are cyclic molecules consisting of six to eight glucose units that are known to form inclusion compounds with various compounds.[3] However, there are few reports on the preparation of inclusion compounds of transition-metal complexes with CDs, although there are some reports on the suggestions of the interactions between CDs and organometallic complexes.[4]

In previous papers we reported on the preparation and properties of inclusion compounds with ferrocene and its analogues with CDs.[5] These observations prompted us to examine the interactions of CDs with olefin–metal complexes which are used as catalysts in a variety of organic syntheses.

We used CDs as inclusion catalysts for reactions catalyzed by transition-metal complexes in aqueous organic two-phase systems.[6] We found that terminal olefins are oxidized to ketones under mild conditions by using palladium chloride and cyclodextrins as catalysts. In this system CDs initially form inclusion compounds with substrates, extracting them from the organic phase to the aqueous phase and allowing them to form complexes with palladium chloride. Then, the substrates undergo oxidation to yield the corresponding ketones. We proposed that ternary complexes, that is, complexes of metal, olefin, and CD, are intermediates in this reaction. Therefore we attempted to prepare and isolate the inclusion compounds

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Table I. Preparation of Inclusion Compounds of Cyclic Olefin Rhodium Complexes

			product		
			Rh, %		
guest	CD	yield, %	found	calcd	CD:guest
$[Rh(\mu\text{-}Cl)(COD)]_2$	α	0			
	β	90	7.9	7.4	2:1
	γ	29	6.5	6.6	2:1
$[Rh(\mu\text{-}Cl)(NBD)]_2$	α	0			
	β	100			2:1
	γ	0			
$[Rh(\mu\text{-}Br)(COD)]_2$	α	0			
	β	70	7.5	7.2	2:1
	γ	58	7.0	6.5	2:1
$[Rh(\mu\text{-}I)(COD)]_2$	α	0			
	β	91	6.5	6.9	2:1
	γ	60	6.6	6.3	2:1
$Pt(COD)Cl_2$	α	0			
	β	99	4.9[a]	4.6[a]	1:1
	γ	0			
$Pt(COD)Br_2$	α	0			
	β	100	9.9[a]	10.0[a]	1:1
	γ	14	11.1[a]	9.1[a]	1:1
$Pt(COD)I_2$	α	0			
	β	90	17.2[a]	14.9[a]	1:1
	γ	100	13.9[a]	13.7[a]	1:1

[a] % halogen.

of olefin–metal complexes with CDs. We chose cyclic olefins, such as cycloocta-1,5-diene and norbornadiene as first-sphere coordinating ligands, because they form relatively stable complexes with transition metals. We found that β- and γ-cyclodextrin form inclusion compounds with some olefin–transition-metal complexes and reported the results briefly in a communication.[7] We describe here the preparation and properties of the inclusion compounds of neutral cycloocta-1,5-diene- and norbornadiene–transition-metal complexes in detail, and the modes of inclusion are discussed.

Results and Discussion

Preparation of Inclusion Compounds. $[Rh(\mu\text{-}Cl)(COD)]_2$ is almost insoluble in water. We found that the addition of β-CD results in the solubilization of $[Rh(\mu\text{-}Cl)(COD)]_2$ in water as shown in the appearance of yellow color in solution, indicating the formation of inclusion compounds in aqueous solutions. When the saturated aqueous solution of β-CD was used, the inclusion compounds formed in the solid state. γ-CD shows smaller effects on the solubilization of $[Rh(\mu\text{-}Cl)(COD)]_2$. α-CD shows no solubilizing effects. Inclusion compounds of olefin–metal complexes with CDs were prepared by adding fine crystals of complexes to a saturated aqueous solution of CD at 40 °C with stirring. In the synthesis of the inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ a 2 M excess of β-CD was added to the reaction mixture. The product that precipitated was washed with water to remove the remaining CD and dried *in vacuo*. Nonincluded metal complexes were removed by washing the residue with tetrahydrofuran. During this process, the included guest was not liberated from the CD cavity. The product was recrystallized from water or aqueous ethanol. All of the inclusion compounds were pale yellow crystals except for those of $(COD)PtCl_2$, which were off-white. The inclusion compounds are soluble in water, ethylene glycol, dimethyl sulfoxide, and dimethylformamide. $[Rh(\mu\text{-}Cl)(COD)]_2$ decomposes slowly in dimethyl sulfoxide.

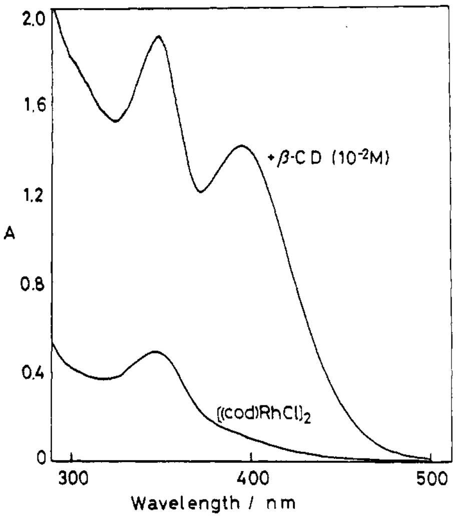

Figure 1. Absorption spectra of $[Rh(\mu\text{-}Cl)(COD)]_2$ in the presence of β-CD.

Table I shows results on the preparation of inclusion compounds of CD–olefin–metal complexes. β-CD formed a 2:1 (CD:guest) inclusion compounds with bis(μ-chloro)bis(cycloocta-1,5-diene)dirhodium, $[Rh(\mu\text{-}Cl)(COD)]_2$, and bis(μ-chloro)bis(norbornadiene)dirhodium, $[Rh(\mu\text{-}Cl)(NBD)]_2$, in high yields. γ-CD formed 2:1 inclusion compounds with $[Rh(\mu\text{-}Cl)(COD)]_2$ in 29% yield, but it did not form inclusion compounds with $[Rh(\mu\text{-}Cl)(NBD)]_2$ which is smaller than $[Rh(\mu\text{-}Cl)(COD)]_2$. It is noteworthy that $[Rh(\mu\text{-}Cl)(NBD)]_2$ was specifically included only in β-CD cavity. β-CD also formed inclusion compounds with dihalo(cycloocta-1,5-diene)platinum, $Pt(COD)X_2$ (X = Cl, Br, I) in high yields. γ-CD formed inclusion compounds with $Pt(COD)I_2$ quantitatively, while it did not form inclusion compounds with $Pt(COD)Cl_2$, and with $Pt(COD)Br_2$ it gave inclusion compounds in a low yield, indicating that γ-CD appears to discriminate the size of the guest compounds, and especially the halogen part.

We could not obtain inclusion compounds of any neutral olefin–metal complexes tested with α-CD. Stoddart et al. recently reported the preparation and structure of an ionic complex, α-CD–$[Rh(COD)(NH_3)_2][PF_6]\cdot 6H_2O$.[8] According to the report $[Rh(COD)(NH_3)_2][PF_6]\cdot 6H_2O$ is positioned almost exactly over the center of the torus in α-CD. One of the two ethylene groups is inserted, and NH_3 groups are hydrogen-bonded with secondary hydroxyl groups of α-CD. This hydrogen bond should be the driving force for the formation of the adduct. We studied the interactions of $[Rh(\mu\text{-}Cl)(COD)]_2$ and α-CD. There was no sign of an interaction between α-CD and $[Rh(\mu\text{-}Cl)(COD)]_2$. No solubilizing effects were observed. No change in the absorption spectrum and no induced Cotton effects were observed with the neutral complex $[Rh(\mu\text{-}Cl)(COD)]_2$. The examination of CPK models shows that these olefin–metal complexes are a little too large to be fully included in the α-CD cavity.

Stoichiometries were determined by elemental analysis, including atomic absorption analysis of the metal contents, and from their ^1H NMR spectra. All the inclusion compounds obtained in this work were stoichiometric one-to-one or two-to-one (host to guest) complexes, depending on the size of the guest compounds.

Properties of Inclusion Compounds. The inclusion compounds were characterized by elemental analysis and

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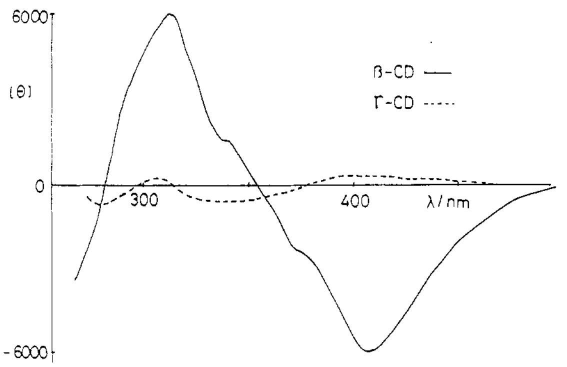

Figure 2. Circular dichroism spectra of β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$ and γ-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$.

Table II. Spectral Data of Inclusion Compounds[a]

inclusn compd	UV λ_{max}, nm (ϵ)	CD θ
2β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$	396 (4500)	405 (−6000)
	345 (2800)	313 (+6000)
	305 (3700)	
2β-CD–$[Rh(\mu\text{-}Br)(COD)]_2$	390 (550)[b]	410 (−300)[b]
	350 (1300)[b]	355 (−300)[b]
		310 (+900)[b]
2β-CD–$[Rh(\mu\text{-}Cl)(NBD)]_2$	375 (1600)	380 (+1300)
	295 (5100)	315 (+1800)
	243 (15000)	
β-CD–$Pt(COD)Cl_2$	305 (420)	325 (+500)
	260 (2900)	263 (+4500)
	220 (9000)	230 (−4800)
β-CD–$Pt(COD)Br_2$	320 (1000)	330 (+950)
	264 (3700)	282 (+3500)
	230 (13000)	245 (−4500)
β-CD–$Pt(COD)I_2$	383 (2000)	380 (−600)
	285 (2800)	300 (−1000)
	260 (3600)	

[a] In H_2O. [b] In ethylene glycol.

their IR, UV, and ^1H NMR spectra. Although $[Rh(\mu\text{-}Cl)(COD)]_2$ is almost insoluble in water, the inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ with β-CD is soluble. Figure 1 shows the absorption spectrum of $[Rh(\mu\text{-}Cl)(COD)]_2$ solubilized by β-CD in aqueous solution. $[Rh(\mu\text{-}Cl)(COD)]_2$ was found to be strongly solubilized by β-CD. The spectrum of the inclusion compound was different from that of the nonincluded $[Rh(\mu\text{-}Cl)(COD)]_2$. A new peak appeared at 400 nm, indicating that the electronic structure of $[Rh(\mu\text{-}Cl)(COD)]_2$ was modified by being included in the β-CD cavity. This may be due to the influence of outer-sphere coordination (e.g. solvent) or some participation of the OH group of CD in the coordination.

Figure 2 shows the circular dichroism spectra of $[Rh(\mu\text{-}Cl)(COD)]_2$ in the presence of β-CD and γ-CD. A large induced Cotton effect was observed in the presence of β-CD, while a very weak induced Cotton effect was observed with γ-CD. These results indicate that the guest compound is well-inserted in the β-CD ring. Spectral data of inclusion compounds are summarized in Table II.

Figure 3 shows the ^1H NMR spectra of β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$. The ^1H NMR spectrum of the inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ with β-CD in the D_2O showed two sets of resonances for apparently two different CD species. One of them is superimposable with that of free β-CD, and the other, which could represent complexed CD, showed large shifts of the signals for H1, H2, and H5 of β-CD to lower frequencies and a shift for H3 to a higher frequency.

The inclusion compounds are thermally stable. The inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ with β-CD, for example, did not liberate the guest when heated to 200 °C in vacuo. Under these conditions the olefin complex sublimes. Figure 4 shows results of thermogravimetric analyses of the inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ with β-CD. The inclusion compound is stable up to 280 °C and decomposed at around the melting point (decomposing point) of β-CD. These results indicate that the olefin–metal complex is tightly included in β-CD cavity. The decomposing points and ^1H NMR data of inclusion compounds are summarized in Table III. Olefin–metal complexes included in the CD cavity could be recovered in high yields by refluxing aqueous ethanol solutions of the inclusion complexes.

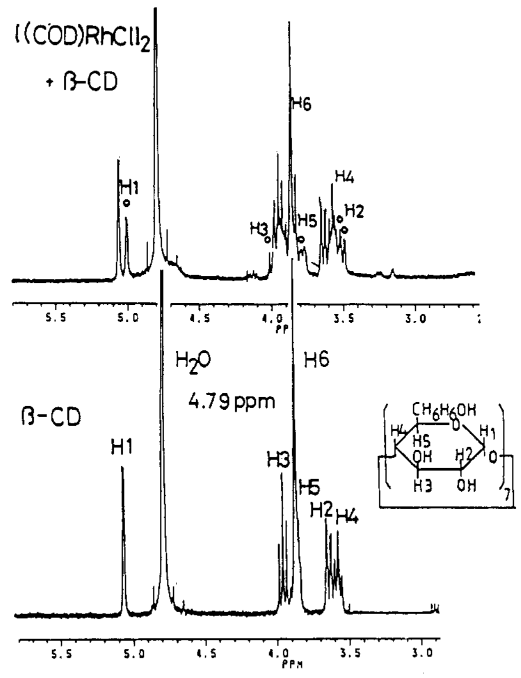

Figure 3. ^1H NMR spectra of β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$.

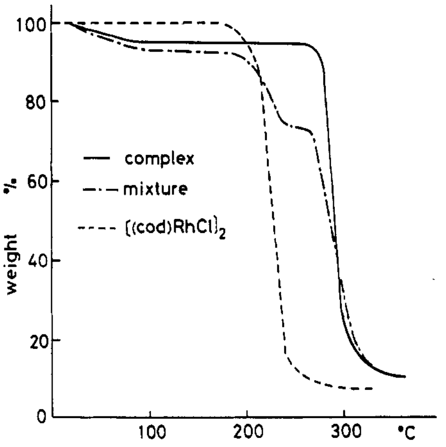

Figure 4. Thermogravimetric analysis of the inclusion compound of $[Rh(\mu\text{-}Cl)(COD)]_2$ with β-CD.

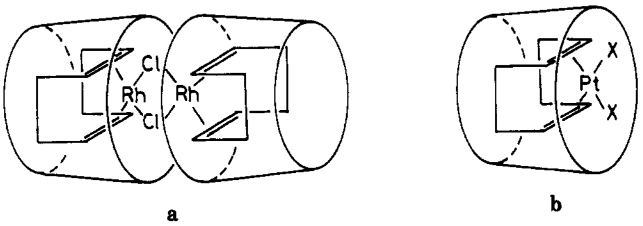

Figure 5. Proposed structures of (a) 2β-CD–$[Rh(\mu\text{-}Cl)(COD)]_2$ and (b) γ-CD–$Pt(COD)X_2$ (X = Cl, Br, I).

Table III. ^{1}H NMR Spectral Data and Decomposing Points of Inclusion Compounds

inclusn compd	decomp point, °C	^{1}H NMR δ (ppm)
2β-CD–[Rh(μ-Cl)(COD)]$_2$	275–280	1.9–2.5 (m, CH_2, 16 H), 4.47 (s, CH=CH, 8 H)
2γ-CD–[Rh(μ-Cl)(COD)]$_2$	260–270	1.9–2.5 (m, CH_2, 16 H), 4.47 (s, CH=CH, 8 H)
2β-CD–[Rh(μ-Br)(COD)]$_2$	260–265	2.0–2.5 (m, CH_2, 16 H), 4.50 (s, CH=CH, 8 H)
2γ-CD–[Rh(μ-Br)(COD)]$_2$	220–243	2.0–2.5 (m, CH_2, 16 H), 4.50 (s, CH=CH, 8 H)
2β-CD–[Rh(μ-I)(COD)]$_2$	250–260	2.0–2.5 (m, CH_2, 16 H), 4.50 (s, CH=CH, 8 H)
2γ-CD–[Rh(μ-I)(COD)]$_2$	200–236	2.0–2.5 (m, CH_2, 16 H), 4.50 (s, CH=CH, 8 H)
2β-CD–[Rh(μ-Cl)(NBD)]$_2$	260–263	1.35 (s, CH_2, 4 H),3.85 (s, CH=CH, 8 H)
β-CD–Pt(COD)Cl_2	255–260	2.1–2.7 (m, CH_2, 8 H), 5.52 (t, CH=CH, 4 H)
β-CD–Pt(COD)Br_2	255–260	2.0–2.7 (m, CH_2, 8 H), 5.58 (CH=CH, 4 H)
γ-CD–Pt(COD)Br_2	251–255	2.0–2.7 (m, CH_2, 8 H), 5.58 (CH=CH, 4 H)
β-CD–Pt(COD)I_2	265–270	1.8–2.5 (m, CH_2, 8 H), 5.70 (t, CH=CH, 4 H)
γ-CD–Pt(COD)I_2	254–260	1.8–2.5 (m, CH_2, 8 H), 5.70 (t, CH=CH, 4 H)

According to CPK molecular models, cycloocta-1,5-diene– and norbornadiene–metal complexes appear to fit well into the β-CD cavity as shown in Figure 5, whereas [Rh(μ-Cl)(NBD)]$_2$ and Pt(COD)Cl_2 are too small to fit in the γ-CD cavity. [Rh(μ-Cl)(COD)]$_2$ and Pt(COD)X_2 (X = Br, I) are large enough to fit in the γ-CD cavity. Proposed structures for the 2β-CD–[Rh(μ-Cl)(COD)]$_2$ and γ-CD–Pt(COD)X_2 are shown in Figure 5.

Experimental Section

Materials. Cyclodextrins (α-CD, β-CD, and γ-CD) were obtained from Hayashibara Biochemical Laboratories Inc. They were purified by recrystallization from water, and their purities were checked by elemental analysis and optical rotation. (Cycloocta-1,5-diene)rhodium chloride dimer was prepared from cycloocta-1,5-diene and rhodium chloride by a procedure similar to that described previously.[9] (Cycloocta-1,5-diene)platinum dichloride was prepared by the procedure described previously.[10] (Cycloocta-1,5-diene)platinum dibromide and diiodide were prepared by the treatment of (cycloocta-1,5-diene)platinum dichloride with excess potassium bromide or potassium iodide.

Table IV. Analytical Data of the Inclusion Compounds of Olefin–Metal Complexes[a]

inclusn compd	anal. C	H	X
2β-CD–[Rh(μ-Cl)-(COD)]$_2$·4H_2O	42.69 (42.84)	6.89 (6.18)	2.61 (2.52)
2γ-CD–[Rh(μ-Cl)-(COD)]$_2$·4H_2O	41.90 (42.57)	6.87 (6.12)	2.92 (2.24)
2β-CD–[Rh(μ-Br)-(COD)]$_2$·4H_2O	40.77 (41.53)	5.99 (5.99)	4.54 (5.52)
2γ-CD[Rh(μ-Br)-(COD)]$_2$·4H_2O	41.27 (41.41)	6.07 (5.95)	5.32 (4.92)
2β-CD–[Rh(μ-I)(COD)]$_2$·4H_2O	39.70 (40.22)	5.72 (5.80)	7.77 (8.49)
2γ-CD–[Rh(μ-I)(COD)]$_2$·4H_2O	39.79 (40.24)	5.64 (5.78)	6.39 (7.59)
2β-CD–[Rh(μ-Cl)-(NBD)]$_2$·4H_2O	42.32 (42.53)	6.43 (5.82)	2.30 (2.56)
β-CD–Pt(COD)Cl_2	38.77 (38.86)	6.05 (5.60)	4.89 (4.58)
β-CD–Pt(COD)Br_2	37.83 (37.57)	5.47 (5.17)	9.88 (10.00)
γ-CD–Pt(COD)Br_2	39.12 (38.21)	5.89 (5.26)	11.07 (9.07)
β-CD–Pt(COD)I_2	35.96 (35.49)	5.43 (4.88)	17.18 (14.90)
γ-CD–Pt(COD)I_2	36.25 (36.27)	5.24 (5.00)	13.94 (13.68)

[a] Required values are given in parentheses.

Preparation of Inclusion Compounds. The inclusion compound of [Rh(μ-Cl)(COD)]$_2$ with β-CD was prepared by adding fine crystals of the rhodium complex (0.123 g, 0.25 mmol) to a stirred saturated aqueous solution of the β-CD (10H_2O adduct, 0.675 g, 0.5 mmol) at 40 °C. The product that precipitated was washed with water to remove the remaining CD and dried in vacuo. Nonincluded metal complexes were removed by washing the residue with tetrahydrofuran. The product was recrystallized from water or aqueous alcohol to give yellow crystals, yield 90%. For 2β-CD-[Rh(μ-Cl)(COD)]$_2$: mp 275–280 °C dec. Anal. Calcd for $C_{100}H_{172}O_{72}Cl_2Rh_2$: C, 42.84; H, 6.18; Cl, 2.52; Rh, 7.4. Found: C, 42.69; H, 6.89; Cl, 2.61; Rh, 7.9. ^{1}H NMR (DMSO-d_6, 360 MHz): δ 1.9–2.5 (m, CH_2, 16 H), 4.47 (s, CH=CH, 8 H).

Other inclusion compounds were prepared in a similar way. The data of elemental analysis were summarized in Table IV.

Measurements. 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 Bruker 360 MHz spectrometer. Circular dichroism spectra were recorded on a JASCO J-205 spectropolarimeter. Thermogravimetric analysis was made by using a Shimadzu thermal analyzer DT-30. Atomic absorption analysis was made by using a Shimadzu A-610S atomic absorption/flame spectrophotometer.

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