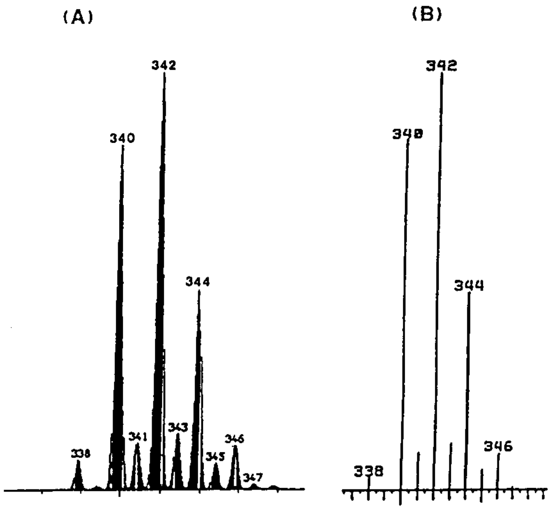
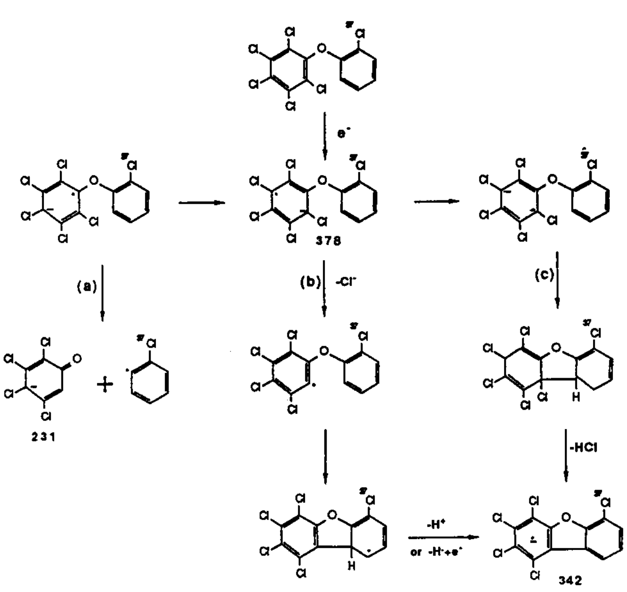


Figure 4. Computer simulated (A) and ECNI mass spectum (B) of [M-HCl]$^-$ ion.



Scheme 2.

requirement to this criterion.[14,15] The photolytic cyclization product of this compound was 1,2,3,4,6-pentachlorodibenzofuran which had the same ^{37}Cl enrichment as [M-HCl]$^-$ cluster has.

In conclusion, the formation of [M-HCl]$^-$ in the ECNI mass spectrometry of 2,2',3,4,5,6-HxCDPE does not involve the loss of *ortho* chlorine and *meta* hydrogen. The concerted dehydrochlorination leading to a cyclized product of pentachlorodibenzofuran (PeCDF) seems to be the probable pathway for the formation of [M-HCl]$^-$.

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Enantioselective Complexation of Amino Ester Salts with Chiral Crown Ether

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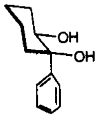
A large number of chiral crown ethers have been prepared for enantioselective recognition of optically active organic guests, usually primary ammonium cations.[1~2] The chirality of the crown ethers was created by introduction of optically pure diols into the macrocyclic ring. The limited diols such as tartaric acid, hydrobenzoin, and diols derived from carbohydrates have been mostly used for the preparation of chiral crown ethers due to synthetic difficulties of the optically pure 1,2-diols.[1] Now, almost all of the chiral *cis*-1,2-diols can be synthesized as an optically pure form through Sharpless's AD method.[3] We were particularly interested in 1-phenyl-*cis*-1,2-cyclohexanediol (**1**) as a chiral building block due to its conformational rigidity, steric environment, and easy availability. In fact, the diol **1** has been already utilized by K. Naemura *et al.* for the preparation of several synthetic hosts including crown ether **2**.[4] Two C_2-symmetric hosts **2** and **3** are composed of the exactly same molecular components, but their structural features are highly different from each other because of the different connecting sequence of the hydroxyl groups (*sec*-OH *vs.* *tert*-OH) of the diol **1**. The CPK molecular models indicate that two identical phenyl or cyclohexyl units in the host **3** are placed in the same side of the crown ether ring and thus it is possible to form a sandwich-type complex with an appropriate guest. We here report, for the first time, the synthesis of the host **3** and its binding properties with amino acid derivatives.



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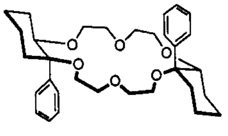
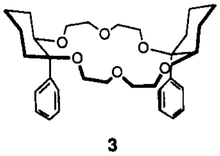


2

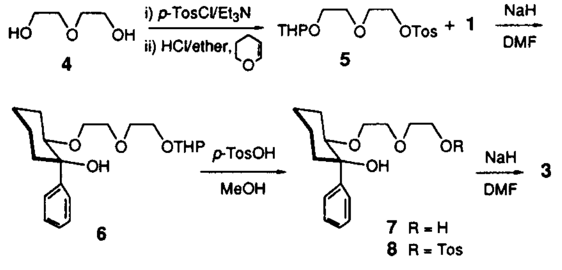


3

The synthesis of the host **3** is outlined in Scheme 1. Optically pure (*R*,*R*)-1-phenyl-*cis*-1,2-cyclohexanediol (**1**) ($[\alpha]_D^{20.5} = +18.9$, $c = 1.29$ in benzene) was prepared from 1-phenylcyclohexene using Sharpless's AD, and followed by twice recrystallization in hexanes/EtOAc.$^{2b\sim c}$ After sequential treatments of diethylene glycol (**4**) with *p*-TosCl/Et_3N (42%) and 3,4-dihydro-2*H*-pyran/HCl (81%), the resulting **5** was coupled with the diol **1** to give compound **6** in a 76% yield. Deprotection of the THP group with *p*-TosOH/MeOH provided compound **7** (79%), in which primary hydroxyl group was selectively protected with *p*-TosCl/Et_3N to give **8** in a 90% yield. Finally, dimerization of the compound **8** in the NaH/DMF afforded the host **3** ($[\alpha]_D^{20.5} = -40.1$, $c = 0.37$ in $CHCl_3$) in a 24% yield.

First, we examined the alkali metal-binding properties of the host **3** by two phase (water/CH_2Cl_2) picrate extractions.[5] The extraction experiments were performed at 25± 0.5 ℃ by employing 5.0 mL of the host **3** (0.10 mM) in CH_2Cl_2 and 5.0 mL of picric acid (0.10 mM) and MOH (0.10 M) in deionized water. The extraction percentages increase in the order of K^+ (88%)>Rb^+ (77%)>Cs^+ (53%)>Na^+(21%)> Li^+ (3.2%), reflecting that the host **3** contains a cavity size similar to that of the conventional 18-crown-6 which has been well known to bind strongly ammonium cations.

Next, we investigated the enantioselective binding properties of the host **3** with various amino ester salts by liquid-liquid extraction method as previously described.[6] The extractions were carried out by thoroughly mixing a $CDCl_3$ solution (1.0 mL, 3.8 mM of the host **3**) and a D_2O solution (1.0 mL, 0.15 M of racemic amino ester hydrochloride and $LiPF_6$) at 25-0.5 ℃. In all cases studied, ~one equivalent of guest was extracted under these conditions. Since the signal for the α proton of the carbonyl group in the guest was clearly separated by forming two diastereomeric complexes, enantioselectivity could be directly measured by ^1H NMR integration. This suggests that the host **3** can be served as a chiral shift reagent for amino ester salts.[7] The results are summarized in Table 1.

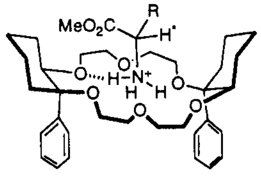


Scheme 1.

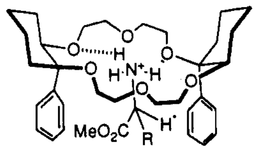
Table 1. Enantiomeric Excess (ee± 2%) of Amino Ester Salts Extracted by Host **3**

Guest	% ee	Guest	% ee
Ala	24	Ile	18
Val	21	Trp	16
Leu	14	Ser	26

The host **3** preferentially binds *L*-enantiomers, but enantioselectivities are relatively low (14-26% ee) and not sensitive to the size of the side chains. This implies that the host **3** is still conformationally flexible due to the presence of four ethylene units and the side chains of the guests are positioned to the side of ethylene glycol units. More structural information on the complex could be obtained from homonuclear NOE difference experiments of a 1 : 1 mixture of L-valine methyl ester hexafluorophophate and the host **3** as a representative example. Irradiation of the α proton (H*) caused enhancements only in the signals for cyclohexane protons and not in those for aryl protons at all. Among two possible structures **9** and **10** of complex, this result indicates that the guest sits on the side of cyclohexyl group in the crown ether ring as shown in complex **9**.



9



10

The origin of enantioselectivity is difficult to analyze at this moment due to a low enantioselectivity ($\Delta\Delta G = 0.17$-0.31 kcal/mol) and a large overlapping of ^1H NMR signals in the complex. We are currently investigating a possibility of the host **3** to form a molecular tweezer-type complex[8] with an appropriate guest.

Experimental

General. All chemicals were reagent grade. Sodium hydride was used as a 55% dispersion in mineral oil. Dimethylformamide was pre-dried over anhydrous $MgSO_4$, distilled under reduced pressure, and then stored over 4 Å molecular sieves. Dichloromethane and triethylamine were distilled from CaH_2 under N_2 atmosphere, Water was deionized and distilled. Sodium hydride was used as a 55% dispersion in mineral oil. Optically pure (*R*,*R*)-1-phenyl-*cis*-1,2-cyclohexanediol (**1**) was prepared according to a literature procedure described by Sharpless.$^{2b\sim c}$ Column chromatography was performed on silica gel 60 (E. Merck, particle size 0.040-0.063 mm, 230-400 ASTM). Ultraviolet Measurements were made with a Shimadzu UV 160A. Melting points were measured on a Laboratory Devices, USA Mel-Temp II and are uncorrected. Infrared spectra were taken on a Nicolet Impact 400 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker DPX 250 MHz (^{1}H) using Me_4Si or $CDCl_3$ as an internal standard.

Compound 6. To a solution of (*R,R*)-1-phenyl-*cis*-1,2-cyclohexanediol (**1**, 1.5 g, 7.7 mmol) in dry dimethylformamide (DMF, 60 mL) containing NaH (55% oil dispersion, 0.5 g, 1.5 equiv) was added ethylene glycol monotetraahydropyran monotosylate (**5**, 3.3 g, 1.2 equiv) under N_2 atmosphere. The resulting solution was heated at 75-80 ℃ overnight (~17 h) and concentrated under reduced pressure. The residue was taken up in EtOAc (30-50 mL) and washed with water, saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography (EtOAc/CH_2Cl_2 1 : 1) to afford **6** (2.2 g, 76%) as a colorless oil: $[\alpha]_D^{20.5}=-20.1$ (c=0.37 in $CHCl_3$); IR (NaCl, neat) 3453, 2940, 1446, 1267, 1110, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, *J*=7.4 Hz, 2H), 7.33 (t, *J*=7.6 Hz, 2H), 7.22 (m, 1H), 4.59 (m, 1H), 3.88-3.81 (m, 1H), 3.75-3.69 (m, 2H), 3.51-3.32 (m, 7H), 3.22-3.17 (m, 1H), 2.81 (s, 1H, OH), 2.00-1.31 (m, 14H).

Compound 7. A solution of **6** (1.8 g, 4.9 mmol) in MeOH (50 mL) containing *p*-toluenesulfonic acid (0.2 g) was stirred overnight at room temperature. The solution was concentrated and the residue purified by column chromatography ((EtOAc/CH_2Cl_2 1 : 1) to give **7** (1.1 g, 79%) as a colorless oil: $[\alpha]_D^{20.5}=-22.7$ (c=0.37 in $CHCl_3$); IR (NaCl, neat) 3453, 2941, 1446, 1267, 1096, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, *J*=7.1 Hz, 2H), 7.34 (t, *J*=7.5 Hz, 2H), 7.25 (m, 1H), 3.73-3.70 (m, 1H), 3.56-3.51 (m, 3H), 3.50-3.31 (m, 4H), 3.21-3.14 (m, 1H), 2.85 (s, 1H, OH), 2.12 (s, br, 1H, OH), 1.99-1.31 (m, 8H).

Compound 8. To a solution of **7** (1.0 g, 3.9 mmol) and *p*-toluenesulfonyl chloride (0.82 g, 1.2 equiv) in dry CH_2Cl_2 (30 mL) was slowly added triethylamine (0.8 mL, 1.5 equiv) at 0 ℃ under N_2 atmosphere. The solution was slowly warmed up to room temperature and stirred for 15 h. The solution was washed with 1 N HCl, water, saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc 2 : 1) to afford **8** (1.40 g, 90%) as a colorless oil: $[\alpha]_D^{20.5}=-14.4$ (c=0.37 in $CHCl_3$); IR (NaCl, neat) 3553, 2947, 1460, 1177, 1110, 926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.78 (d, *J*=8.3 Hz, 2H), 7.47-7.15 (m, 7H), 3.93 (t, *J*=4.7 Hz, 2H), 3.69-3.63 (m, 1H), 3.41-3.14 (m, 6H), 2.66 (s, 1H, OH), 2.45 (s, 3H), 1.90-1.35 (m, 8H).

Host 3. A solution of **8** (1.35 g, 3.1 mmol) and NaH (55% oil dispersion, 0.25 g, 2 equiv) in dry DMF (20 mL) was heated at 75-80 ℃ overnight (~11 h) and concentrated under reduced pressure. The residue was taken up in EtOAc (30-50 mL) and washed with water, saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography (acetone/CH_2Cl_2 1 : 2) to afford the host **3** (0.20 g, 24%) as a colorless solid: mp 69-70 ℃; $[\alpha]_D^{20.5}=-40.1$ (c=0.37 in $CHCl_3$); IR (NaCl, neat) 2941, 1460, 1177, 1096, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.50-7.47 (m, 4H), 7.23-7.20 (m, 6H), 3.71-3.63 (m, 4H), 3.60-3.34 (m, 12H), 3.18-3.11 (m, 2H), 2.04-1.26 (m, 16H); ^{13}C NMR ($CDCl_3$) δ: 143.2, 127.7, 127.3, 126.5, 83.2, 79.9, 70.5 (2 carbons), 69.3, 62.1, 35.9, 26.5, 24.4, 21.3.

Extraction of Alkali Metal Cations. A CH_2Cl_2 solution (0.10 mM) of the host **3** and an aqueous solution containing picric acid (0.10 mM) and MOH (0.10M) were separately prepared and allowed to stand for at least 2 h at 25± 0.5 ℃. Equal volume (5.0 mL) of each solution was placed in a stoppered glass tube and vigorously agitated for 2 min on a Vortex mixer (GW-92VM). The two-layer solution was centrifuged for 10 min at high speed and allowed to stand for 1 h at 25± 0.5 ℃ to complete phase separation. The % extractions were calculated by differences in the absorbance of the picrate ion in aqueous layer before and after extractions.

Determination of Enantioselective Complexation. To a test tube were added a $CDCl_3$ solution (1.0 mL) of the host **3** and a D_2O solution (1.0 mL) containing racemic amino ester ammonium hydrochloride (0.15 M) and $LiPF_6$ (0.15 M). The mixture was vigorously agitated for 1 min on a Vortex mixer (GW-92VM). The two-layer solution was centrifuged for 10 min at high speed and allowed to stand for 1 h at 25± 0.5 ℃ to complete phase separation. An aliquot (600 μL) of the $CDCl_3$ solution was carefully withdrawn and subjected to ^{1}H NMR analysis. The enantiomeric excess (ee) was calculated by ^{1}H NMR integral of the signal for the a proton to the carbonyl in the guest, and assignment of configuration was made by direct comparisons of the chemical shifts with those of a pure L-complex or D-complex.

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Isolation and X-ray Structure of a Discrete Five-Coordinate Na(I) Complex Containing CpCo-P(OMe)$_2$(=O)}$_3$$^-$ Ligands

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The anionic Cobalt(III)-based oxygen tripodal ligand L_{OEt} (L_{OEt}=[CpCo{P(=O)(OEt)$_2$}$_3$]$^-$), developed by Kläui and coworkers, can form stable complexes with various transition metals.[1] La(III), Y(III) complexes of L_{OMe} (L_{OMe}=[CpCo{P(=O)(OMe)$_2$}$_3$]$^-$) have been studied in order to compare with middle or late transition metal complexes containing the ligand in our laboratory.[2~3] Also attempts to isolate Zr(L_{OMe})$_2$Cl$_2$ from the feasible reaction of ZrCl$_4$ with 2 equivalent NaL_{OMe} gave the formation of the unusual dimer in an unusual bridging fashion of tripodal ligands, (L)Zr(L)$_2$Zr(L) (L=CpCo{P(=O)(OMe)$_2$}$_2${P(=O)(OMe)(O)}),[4] in which L_{OMe} was modified by the labile chlorides at Zr(L_{OMe})$_2$Cl$_2$ as an intermediate. Therefore, we tried to synthesize (L_{OMe})$_2$Zr(amide), which would be an useful candidate for the catalyst of hydroamination of alkyne,[5] by reaction of Zr(L_{OMe})$_2$Cl$_2$ with excess amine. However, we isolated a discrete five-coordinate Na(I) complex containing L_{OMe} instead of the disired product. In this paper we describe the crystal structure of the complex. Its structure is distinguishable from that of NaL_{OEt} that is a trimeric aggregate with two water molecules.[6]

Experimental

All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature. All solvents were purified by standard methods and were freshly dried and distilled prior to use. ZrCl$_4$ was purchased from Aldrich Co. and used as·received, *tert*-Buthyl amine or diethylamine was dried over KOH and distilled under an argon atmosphere. L_{OMe} was prepared by the literature method.[7]

^{1}H NMR spectra were obtained in CDCl$_3$ and referenced to internal deuterated solvent and recalculated relative to TMS on a Bruker AM-300 spectrometer. Elemental analyses were carried out by the Chemical Analysis Laboratory at Center for Scientific Instruments of Kyungpook National University.

Preparation of (L_{OMe})$_2$Na·H$_3$NC(CH$_3$)$_3$·[H$_3$NC(CH$_3$)$_3$]Cl. To a mixture of ZrCl$_4$ (0.15 g, 0.6 mmol) and NaL_{OMe} (0.50 g, 1.2 mmol) 50 mL of THF was introduced. The mixture was stirred for 2 days at room temperature to afford yellow solution and white precipitate, NaCl and then H$_2$NC(CH$_3$)$_3$ (0.307 g, 4.2 mmol) was added to the mixture solution. This mixture was stirred for 1 day at room temperature. Volatile materials were removed under reduced pressure. Extraction of the solid with benzene afforded a yellow solution. The solution was concentrated and left at room temperature to yield the yellow crystalline product (0.47 g, 70%).

Anal. Calcd for $C_{30}H_{70}ClCo_2N_2NaO_{18}P_6$: C, 32.49; H, 6.36. Found: C, 31.83; H, 6.34. ^{1}H NMR (C$_6$D$_6$): δ 5.13 (s, C$_5$H$_5$, 5H), δ 3.73 (m, (MeO)$_2$P(O)-, 18H), δ 1.40 (s, (Me$_3$C-, 9H), δ 8.91 (b, H$_3$N-, 3H).

X-ray crystallographic analysis. An X-ray quality single crystal, 0.45×0.40×0.35 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with MoKα radiation (λ=0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections (18°<2θ<26°). Intensity data were collected with θ range of 2.37-25.37° in ω/2θ scan mode. Three standard reflections were monitored every 1h during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with Ψ scans were applied to the data. The structure was solved by using direct method and refined by full-matrix least-squares techniques on F^2 using SHELXS-86[8] and SHELXL-93.[9] All non-hydrogen atoms were refined by using anisotropic thermal factors except disodered C atoms of Cp rings, and all hydrogen atoms were positioned geometrically and refined using riding model. The final cycle of the refinement converged with R_1=0.055 and wR_2=0.129. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Relative bond distances and angles are tabulated in Table 2.

Results and Discussion

Reaction of ZrCl$_4$ with 2 equivalent NaL_{OMe} in the THF at room temperature followed by addition of excess H$_2$NC(CH$_3$)$_3$, removal of precipitate and then evaporation of volatile material affords a yellow crystalline product. The ^{1}H NMR spectrum of the product exhibits the resonances of phosphonate methyl, Cp, and *tert*-buthyl groups. From the integrations of the peaks for Cp rings and *tert*-buthyl groups we found 1 : 1 ratio between the two groups. It was very wondering fact that two L_{OMe} and two *tert*-buthyl amines were bound to Zr atom. Therefore, an X-ray crystal structure analysis was carried out. The crystal structure surprisingly shows Na(L_{OM})$_2$ H$_3$NC(CH$_3$)$_3$$^+$ and co-crystallized [H$_3$NC(CH$_3$)$_3$]Cl