

Chiral Recognition with Crown Ethers Having Planar Chiral (η^4 -Diene)tricarbonyliron Moieties

Hiroshi Yamaguchi, Saburo Nakanishi, Nobuhiro Kihara, and Toshikazu Takata*
 Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
 1-1 Gakuen-cho, Sakai, Osaka 599-8531

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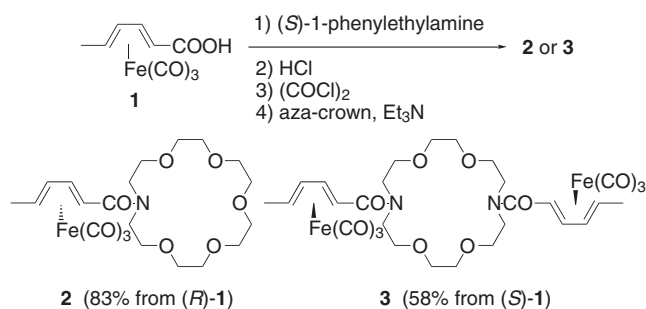
Crown ethers with a planar chiral (1,3- η^4 -diene)tricarbonyliron unit were prepared. They revealed a good chiral recognition ability for α -substituted benzylammonium salts ($K_{rel} = 1.3$ – 2.0). Ligand substitution of the iron tricarbonyl moiety with triphenylphosphane inverted the chiral selectivity.

Artificial host molecules that recognize chirality have been extensively studied. While various chiral crown ethers have been introduced as effective chiral recognition sites,¹ Cram demonstrated that crown ethers with an axially chiral unit are among the most effective host molecules to discriminate enantiomers of primary ammonium salts.² Given that planar chirality provides an equally effective chiral environment as axial chirality,³ crown ethers with a planar chiral unit can also be expected to show effective chiral recognition ability. However, so far, there have not been any reports of crown ethers with a planar chiral unit.^{2c} Planar chiral tricarbonyliron ($\text{Fe}(\text{CO})_3$) complexes of unsymmetrical 1,3-diene have been extensively used for asymmetric organic synthesis due to their chemical stability, effective chiral environment based on the bulkiness of the $\text{Fe}(\text{CO})_3$ unit, no racemization, and availability of optically active complexes.⁴ Further, the $\text{Fe}(\text{CO})_3$ complex undergoes a ligand substitution reaction which enables to modify the steric and electronic environments of the complexes. Since the (η^4 -diene) $\text{Fe}(\text{CO})_3$ complex is inert to various functional groups, crown ethers with a planar chiral (η^4 -diene) $\text{Fe}(\text{CO})_3$ moiety are expected to constitute a novel type of host molecules able to recognize the chirality of functional ammonium salts. In this paper, we wish to report the preparation and chiral recognition ability of novel crown ethers having a planar chiral (η^4 -diene) $\text{Fe}(\text{CO})_3$ unit.

The syntheses of crown ethers **2** and **3** with planar chiral (η^4 -diene) $\text{Fe}(\text{CO})_3$ units are demonstrated in Scheme 1. Both enantiomers of carboxylic acid **1** were obtained in the optically pure form by fractional crystallization of their (*S*)-1-phenylethylammonium salts.⁵ The conversion of (*R*)-**1** to the corresponding acid chloride followed by aminolysis with 1-aza-18-crown-6 gave planar chiral crown ether **2** in 83% yield. Using the same procedure, bifunctional crown ether **3** having two planar chiral iron complex units was obtained from 1,10-diaza-18-crown-6 and (*S*)-**1** in 58% yield.⁶

The association constants (K_a) of **2** and **3** with both enantiomers of α -substituted benzylammonium picrates **4** and **5** were measured in CDCl_3 at 24 °C by solid-liquid extraction method.⁷ The results are summarized in Table 1. The chiral recognition ability of the crown ethers was evaluated by the ratio (K_a for **4**)/(K_a for **5**), which is denoted by K_{rel} .

Crown ether **2** recognized **4** more preferentially than **5** ($K_{rel} = 1.31$ – 1.37). Thus, the high chiral recognition ability of crown



Scheme 1.

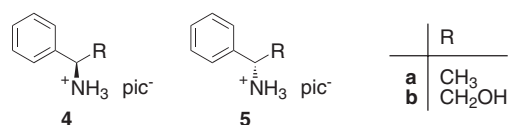


Table 1. Association constant (K_a) of the planar chiral crown ethers with α -substituted benzylammonium picrates^a

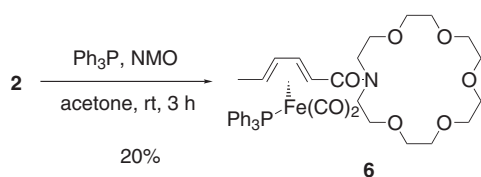
Entry	Host	Guest	R	K_a for 4 /L·mol ⁻¹	K_a for 5 /L·mol ⁻¹	K_{rel}^b
1	2	a	CH_3	8.9×10^2	6.8×10^2	1.31
2	2	b	CH_2OH	8.9×10^1	6.5×10^1	1.37
3	3	a	CH_3	4.1×10^1	8.6×10^1	0.47
4	6	a	CH_3	9.6×10^2	1.3×10^3	0.77

^aMeasured by solid-liquid extraction of ammonium picrate into CDCl_3 by the addition of crown ethers. ^b $K_{rel} = (K_a \text{ for } \mathbf{4}) / (K_a \text{ for } \mathbf{5})$.

ethers having planar chirality was confirmed. Since the K_a s of **2** with **4b** or **5b** were smaller than those with **4a** and **5a**, the hydroxy group in R did not contribute to the complexation by hydrogen bonding, but probably acted as a sterically hindered group. When crown ether **3** was used as a host compound, a higher chiral recognition ability than **2** was observed (entry 1: $K_{rel} = 1.31$, entry **3**: $1/K_{rel} = 2.13$). As the planar chirality of **3** is opposite to that of **2**, **3** preferentially recognized **5** rather than **4**. The synergistic effect of two (η^4 -diene) $\text{Fe}(\text{CO})_3$ units in **3** presumably enhanced the chiral recognition ability. The C_2 symmetric structure of **3** apparently contributed to the synergistic effect. However, **3** showed rather low K_a values as compared to **2**, undoubtedly because of the electron-withdrawing nature and the steric hindrance of the (η^4 -diene) $\text{Fe}(\text{CO})_3$ unit.

The (η^4 -diene) $\text{Fe}(\text{CO})_3$ complex easily reacts with phosphane to give (η^4 -diene) $\text{Fe}(\text{CO})_2\text{L}$ (L = phosphane). Because of the electron-donating nature of phosphane ligands,⁸ crown ethers having a (η^4 -diene) $\text{Fe}(\text{CO})_2\text{L}$ moiety are expected to be better hydrogen-bonding acceptors than those having a (η^4 -

diene)Fe(CO)₃ moiety. Further, the steric bulkiness of phosphane can provide a higher ordered recognition site. Thus, crown ether **6** was synthesized from (*R*)-**2** by ligand substitution reaction with triphenylphosphane (Scheme 2).⁹



Scheme 2.

As expected, **6** showed higher K_a values for **4a** and **5a** than **2**, as shown in Table 1 (entries 1 and 4). Surprisingly, opposite chiral recognition was observed. As the chiral recognition ability of both crown ethers was close (entry 1: $K_{rel} = 1.31$, entry 4: $1/K_{rel} = 1.30$), the substitution by PPh₃, which acted as a chiral handler, simply inverted the chiral selectivity of the crown ether. It is presumed that PPh₃ changed the relative configuration between diene and crown ether moiety to construct the opposite chiral environment on the crown ether plane.

In summary, it was demonstrated that the introduction of planar chirality is a very effective method to construct a crown ether host molecule for chiral recognition. High chiral recognition ability was confirmed in very simple crown ethers having a planar chiral (η^4 -diene)Fe(CO)₃ unit. Further, the ligand exchange of the complex drastically inverted chiral selectivity. Since various planar chiral groups are known, novel host molecules with higher chiral recognition ability will likely be constructed based on planar chirality.

References and Notes

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