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Synthesis, structure and properties of the macrocyclic ferrocenophanes with cyclopentadienyl ligands tethered by oligo(ethylene glycol) chain

Yuji Suzaki, Atsuko Takagi, Kohtaro Osakada*

Chemical Resources Laboratory (Mail Box R1-3), Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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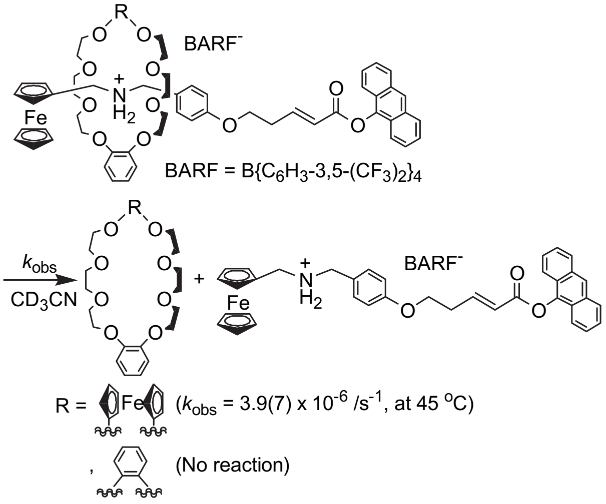
Cyclization reactions of $Fe\{C_5H_4OCH_2(CH_2OCH_2)_nCH_2OTs\}_2$ (n = 1, 2) with C_6H_4-1,2-$(OH)_2$, C_6H_4-1,3-$(OH)_2$, and $Fe(C_5H_4OAc)_2$ under basic conditions yield the corresponding macrocyclic 1,1′-ferrocenophanes. The ferrocenophane having a pyrido-crown ether structure was also synthesized. These ferrocenophanes were characterized by X-ray crystallography and NMR spectroscopy. Cyclic voltammograms of the ferrocenophanes exhibited reversible redox peaks assigned to the oxidation and reduction of the ferrocene unit. The macrocyclic pyrido-containing ferrocenophane forms pseudorotaxane with $[NH_2\{(CH_2)_9Me\}_2]$BARF (BARF = $B\{C_6H_3$-3,5-$(CF_3)_2\}_4$) in $CDCl_3$.

1. Introduction

Ferrocenophanes, ferrocene derivatives whose cyclopentadienyl ligands were connected by bridging unit, have received attention due to their unique propertied such as the intramolecular electronic communication, the ligandation to the transition metals and their ring-opening polymerization [1–5]. Macrocyclic ferrocenophanes having oligo(ethylene glycol) units as the tether of the cyclopentadienyl ligands were regarded as analogues to the crown ethers and have been reported to include metal cations as the host molecule [6]. The affinity to the metal cations varies depending on the length of the oligo(ethylene glycol) tether, oxidation state of the Fe atom, and the presence of a heteroatom within the ring [6–8].

Recently we have reported a macrocyclic octaoxa[22]ferrocenophane and its rotaxane with dialkyl ammonium [9]. The rotaxane undergoes disaggregation reaction in CD_3CN ($k_{obs} = 3.9(7) \times 10^{-6}\ s^{-1}$ at 45 °C) (Eq (1)), although the rotaxane having DB24C8 (dibenzo[24]crown-8) as a macrocyclic component is stable in solution under the same conditions. It is probably assigned to the larger size of the cavity of the octaoxa[22]ferrocenophane than that of DB24C8. The macrocyclic structures of these 1,1′-ferrocenylene-containing crown ethers were considered to influence the formation of the host–guest complexes with the cationic ions or molecules. Akabori reported detailed structure of the complex of a pentaoxa[13]ferrocenophane and NaSCN [6e]. In this paper we report preparation of macrocyclic 1,1′-ferrocenophanes as well as their structures in the solid state, electrochemical properties, and pseudorotaxane formation in solution.



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* Corresponding author. Tel./fax: +81 45 924 5224.
E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

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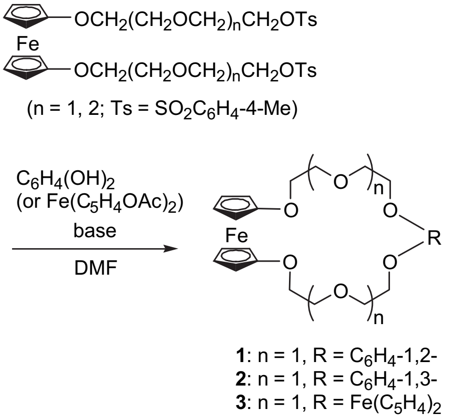

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1: n = 1, R = C_6H_4-1,2-
2: n = 1, R = C_6H_4-1,3-
3: n = 1, R = $Fe(C_5H_4)_2$
4: n = 2, R = C_6H_4-1,2-
5: n = 2 R = $Fe(C_5H_4)_2$

2. Results and discussion

Macrocyclic 1,1′-ferrocenophanes, **1**–**3** and **5**, were newly prepared, although **4** was already reported elsewhere [9]. Fe{$C_5H_4OCH_2(CH_2OCH_2)_nCH_2OTs$}$_2$ (n = 1, 2; Ts = $SO_2C_6H_4$-4-Me) is synthesized by reaction of TsCl and Fe{$C_5H_4OCH_2(CH_2OCH_2)_nCH_2OH$}$_2$ (n = 1, 2) and used for the cyclization shown in Eq (2). Reaction of $Fe(C_5H_4OCH_2CH_2OCH_2CH_2OTs)_2$ and C_6H_4-1,2-$(OH)_2$ with K_2CO_3 in DMF for 7 days yields **1** having a hexaoxa[16]ferrocenophane structure (Table 1). FABMS (Fast atom bombardment mass spectrum) of **1** shows a peak at $m/z = 468$ corresponding to the structure. $^{13}C\{^1H\}$ NMR of **1** contains signals of C_5H_4 units (δ 56.1, 61.8, 126.7). Similar cyclization reactions yield ferrocene-containing crown ether **2**–**5** in 8–88% (Eq (2), Table 1). The reactions of $Fe(C_5H_4OCH_2CH_2OCH_2CH_2OTs)_2$ with C_6H_4-1,2-$(OH)_2$ and C_6H_4-1,3-$(OH)_2$ in the presence of K_2CO_3 yield **1** and **2** in higher yield (**1**:58%, **2**:20%) than those with Cs_2CO_3 (**1**:43%, **2**:13%). The difference in the yields was attributed to the template effect of the macrocycle to inclusion of metal cations, K^+ or Cs^+, which facilitates the cyclization.[10] Ferrocenophanes **3** and **5** were synthesized from the reaction of Fe{$C_5H_4OCH_2(CH_2OCH_2)_nCH_2OTs$}$_2$ (n = 1, 2) with $[Fe(C_5H_4O)_2]^{2-}$, generated in situ from $Fe(C_5H_4OAc)_2$, Cs_2CO_3 and KOH in water. $^{13}C\{^1H\}$ NMR spectrum of **3** contains three signals for C_5H_4 (δ 56.2, 62.1, 127.0) and two signals for OCH_2 (δ 70.1 (overlapping)) due to the symmetric structure composed of two 1,1′-ferrocenylenes and two di(ethylene glycol) units. ^1H NMR spectrum of **3** in $CDCl_3$ shows the two signals of the C_5H_4 hydrogens (δ 3.86–3.89, 4.11) as well as the two signals of OCH_2 (δ 3.86–3.89, 4.06) as shown in Fig. 1(A). Addition of NaBARF (BARF = B{C_6H_3-3,5-$(CF_3)_2$}$_4$) to a $CDCl_3$ solution of **3** ([**3**] = [NaBARF] = 10 mM) causes shift of the signals of OCH_2 (δ 3.86–3.89, 4.06) to lower magnetic field position (δ 4.01, 4.33) and of C_5H_4 (δ 3.86–3.89, 4.11) to the higher magnetic field positions (δ 3.71, 3.92). FABMS of the mixture shows a peak at $m/z = 599$ corresponding to $[\mathbf{3} + Na]^+$. These results indicate that **3** and Na^+ form the 1:1 inclusion complex in $CDCl_3$ solution [6,10].

Table 1
Conditions and yields of macrocyclic ferrocenophanes, **1**–**6**.

Compound	n	R	Base	Time	Isolated Yields
1	1	C_6H_4-1,2-	K_2CO_3	7 days	58%
			Cs_2CO_3	4 days	43%
2	1	C_6H_4-1,3-	K_2CO_3	3 days	20%
			Cs_2CO_3	3 days	13%
3	1	$Fe(C_5H_4)_2$	Cs_2CO_3/KOH	7 h	8%
4[a]	2	C_6H_4-1,2-	Cs_2CO_3	3 days	88%
5	2	$Fe(C_5H_4)_2$	Cs_2CO_3/KOH	19 h	33%
6[b]	–	–	NaH	2 days	18%

[a] Ref. [9].
[b] See Eq. (3) and experimental section for the structure of the compounds and reaction conditions.

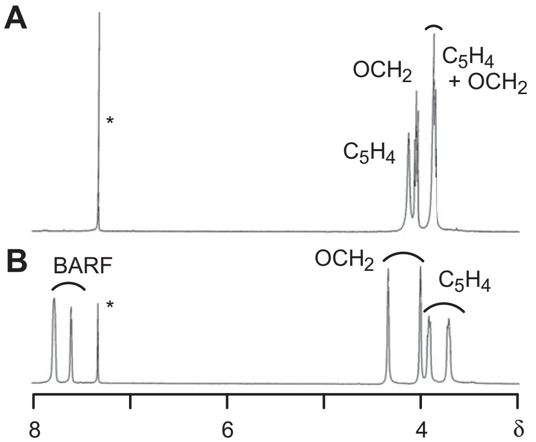
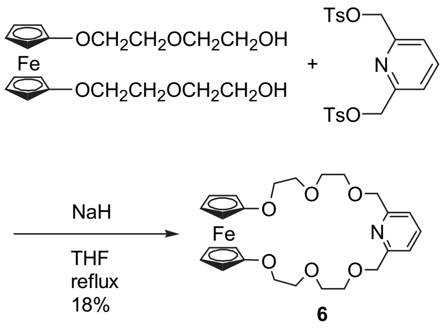


Fig. 1. ^1H NMR spectra (300 MHz, $CDCl_3$, r.t.) of (A) **3** ([**3**] = 10 mM) and (B) **3** and NaBARF ([**3**] = [NaBARF] = 10 mM). Peaks with asterisk indicate $CHCl_3$.

Reaction of $Fe(C_5H_4OCH_2CH_2OCH_2CH_2OH)_2$ with C_5H_3N-2,6-$(CH_2OTs)_2$ in the presence of NaH ($[Fe(C_5H_4OCH_2CH_2OCH_2CH_2OH)_2]$ = [C_5H_3N-2,6-$(CH_2OTs)_2$] = 5 mM) forms the cyclization product **6** in 18% isolated yield (Eq (3)). $^{13}C\{^1H\}$ NMR spectrum of **6** shows signals for the cyclopentadienyl carbons at δ 56.0, 62.9 and 128.8. FABMS of **6** shows a peak at $m/z = 497$ corresponding to the calculated molecular weight.



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(3)

Recrystallization of **1**, **2** and **3** gave the single crystals suitable for X-ray structure analysis. Complexes of **5** with $KBPh_4$ and of **6** with NaBARF were also characterized by X-ray crystallography. The obtained molecular structures were shown in Fig. 2. $C(C_5H_4)$–O bonds of **1** (C5–O1 and C20–O6) adopt almost eclipsed conformation to the axis of the ferrocene unit (Chart 1(A), Table 2). The dihedral angle of the bonds, C5–O1 and C20–O6, is 16°. The conformations of C5–O1–C6 and C20–O6–C19 units avoid the electrostatic repulsion of the lone pairs of O1 and O6. Cyclopentadienyl ligands of **1** are deviated by 6.1(1)° from the ideal parallel conformation (Chart 1(B)) which is partly ascribed to the repulsion of O1 and O6. H8 atom of **1** has a contact with O3 (2.536 Å) which is shorter than the sum of the van der Waals radii for oxygen and hydrogen (2.72 Å), indicating the intramolecular hydrogen bond. Dihedral angles of C_5H_4 and C_6H_4 are almost vertical (86.33(9)° and 88.06(9)°). Distance between Fe1 and the centroid of C_6H_4 is 10.053 (1) Å. The circumferential bond lengths, the sum of the bond lengths of the macrocycle unit containing Fe1–C5–O1– through