End-capping of Pseudo[2]rotaxane Composed of Alkyl(ferrocenylmethyl)ammonium and Dibenzo[24]crown-8 via Cross Metathesis Reactions

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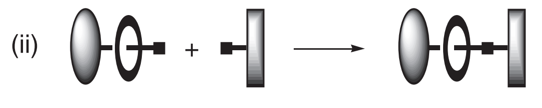
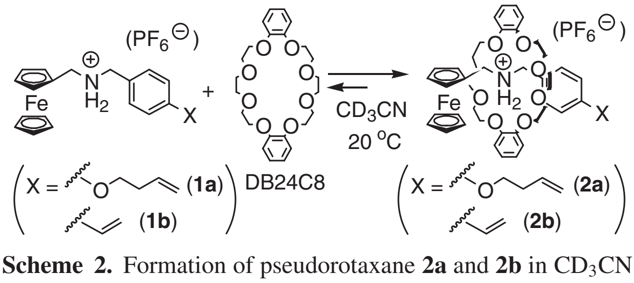
Pseudo[2]rotaxane, having dialkylammonium with a ferrocenyl stopper and a vinyl group as the axis component, underwent cross-metathesis reaction with acrylate esters to form ferrocene-containing [2]rotaxanes.

Rotaxanes have attracted increasing attention because of their interlocked structures as well as their unique physical and chemical properties.[1,2] Since ferrocene derivatives undergo one-electron redox reaction reversibly,[3] they are employed as materials to construct the host–guest systems and rotaxanes that function as the stimulus response system driven by the electrochemical reaction of the ferrocene center.[4,5] Recently, we reported that electrochemical oxidation of aminomethylferrocene derivatives in the presence of TEMPOH (1-hydroxy-2,2,6,6-tetramethylpiperidine) and DB24C8 (dibenzo[24]crown-8) produced the pseudo[2]rotaxanes that contain ferrocenomethylammonium as the axis component.[6] Suitable end-capping reactions of these pseudo[2]rotaxanes would fix the interlocked structure and form the corresponding [2]rotaxanes with bulky stoppers at both ends of the axis molecule, as shown in Scheme 1. Bond forming reactions, such as cycloaddition of azide to alkyne and esterification of acid anhydride with alcohol, were used for end-capping, because they form a new bond between the axis molecule and bulky stopper molecule efficiently under mild conditions.[7] Cross metathesis between the vinyl group and acrylate was recently reported to proceed selectively in the presence of the Ru catalyst. In this paper, we report end-capping of a ferrocene-containing [2]rotaxane via the Ru-catalyzed cross metathesis reaction.[8,9]



Scheme 1. End-capping method for synthesis of [2]rotaxane.



Scheme 2. Formation of pseudorotaxane **2a** and **2b** in CD_3CN.

Scheme 2 shows the preparation of pseudo[2]rotaxanes with a ferrocenyl stopper and a vinyl group. **1a** and **1b** are prepared from ferrocenecarboxaldehyde and benzylamines containing an olefin group.[6,10] Dissolution of an equimolar mixture of **1a** and DB24C8 in CD_3CN (10 mM for each compound) forms pseudo[2]rotaxane **2a**. ^1H NMR signals of NCH_2 hydrogens (δ 4.37, 4.50) were observed at lower magnetic field positions than the corresponding signals of **1a** (δ 4.02, 4.04), suggesting C–H···O interaction between the NCH_2 group and DB24C8, while the signals of vinyl hydrogen of **1a** and **2a** overlapped with each other. A mixture of **1b** and DB24C8 in CD_3CN also forms pseudo[2]rotaxane, **2b**. The ^1H NMR signals of vinyl hydrogens of **2b** (δ 5.22, 5.67, 6.58) shifted to higher magnetic field positions than the corresponding signals of **1b** (δ 5.33, 5.86, 6.77), because of the shielding effect by aromatic groups of DB24C8. The formation of **2a** and **2b** was confirmed also from the electrospray ionization mass spectrometry (ESIMS). Slow diffusion of Et_2O to a CH_2Cl_2 solution of **1b** and DB24C8 leads to growth of the crystals of **2b**. X-ray analysis of **2b** revealed the pseudo[2]rotaxane structure; NH_2 and CH_2 groups of the axis molecule show the presence of N^+–H···O and C–H···O hydrogen bonds (H1–O4, 2.36 Å and H13–O6, 2.35 Å) (Figure 1). Close contact is observed between an aromatic ring of DB24C8 and the axis (C24–C1, 3.92(2) Å).[11] Precise ratios between **1a** (or **1b**) and **2a** (or **2b**) in $CDCl_3$ were not determined due to the low solubility of **1a** (or **1b**), although the solutions in CD_3CN contain equilibrated mixtures of these compounds in a 36/64 (or 43/57) ratio at 20 °C. A cross metathesis reaction of an axis molecule **1a** and 3,5-dimethylphenyl acrylate using Ru catalyst[9] in the presence of DB24C8 gives [2]rotaxane **3**, which is isolated in 72% yield (Scheme 3).[12,13] The trans configuration of the C=C double bond was determined from the ^1H NMR spectrum, which shows a large coupling constant of vinylene hydrogens ($J = 15$ Hz). High trans selectivity in the cross metathesis reactions of terminal olefins with ethyl acrylate was reported.[14] A similar reaction using ferrocenyl acrylate[15] gives [2]rotaxane **4** having two ferrocenyl groups as the stopper. A reaction using **1b** and 3,5-dimethylphenyl acrylate did not form [2]rotaxane

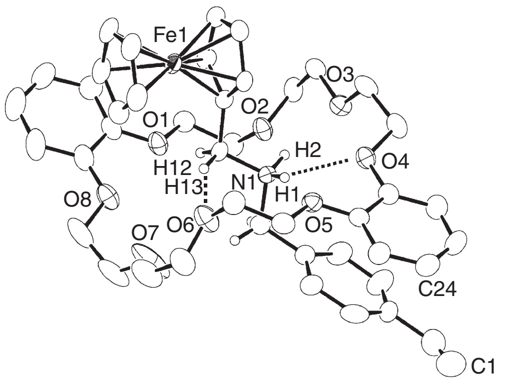
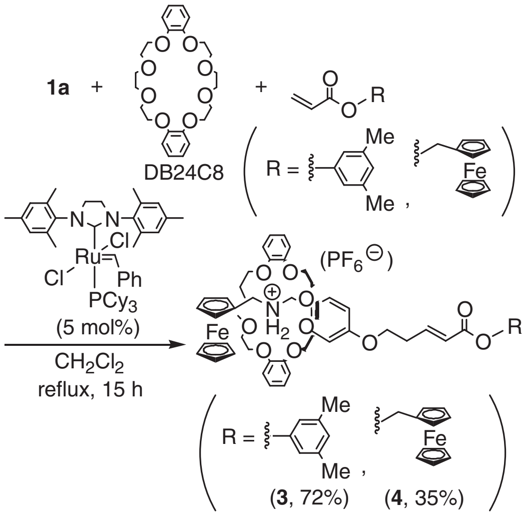


Figure 1. ORTEP drawing of cationic component of **2b**.



Scheme 3. Syntheses of [2]rotaxanes via cross metathesis.

due to steric congestion around the vinyl group by DB24C8 of **2b**.

The cyclic voltammogram of **3** in MeCN shows reversible redox reaction at $E_{1/2} = 0.47\,\mathrm{V}$ (vs $\mathrm{Ag^+/Ag}$, scan rate $= 0.1\,\mathrm{V\,s^{-1}}$). The electrochemical oxidation and reduction of **3** are reversible in the range of scan rates $0.01\text{–}0.25\,\mathrm{V\,s^{-1}}$. The redox potential is the same as that of **1a** ($E_{1/2} = 0.47\,\mathrm{V}$, scan rate $= 0.1\,\mathrm{V\,s^{-1}}$). This result indicates that DB24C8 in **3** interacts more strongly with the ammonium group of the axis molecule than that of neutral [2]rotaxane composed of a ferrocene-containing axis molecule and DB24C8.[5]

In summary, we have demonstrated that cross metathesis reaction can be an efficient method for the preparation of [2]rotaxanes. Studies of reactions to obtain higher order rotaxanes are in progress.

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References and Notes

1 a) *Catenanes, Rotaxanes, and Knots, Organic Chemistry*, ed. by G. Schill, Academic Press, New York, **1971**, Vol. 22. b) *Molecular Catenanes, Rotaxanes and Knots*, ed. by J.-P. Sauvage, C. Dietrich-Buchecker, Wiley-VCH, Weinheim, **1999**.

2 a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. b) Molecular Machines Special Issue: P. F. Barbara, *Acc. Chem. Res.* **2001**, *34*, 409. c) *Molecular Devices and Machines, A Journey into the Nanoworld*, ed. by V. Balzani, M. Venturi, A. Credi, Wiley-VCH, Weinheim, **2003**.

3 *Ferrocenes*, ed. by A. Togni, T. Hayashi, VCH, New York, **1995**.

4 a) A. Harada, S. Takahashi, *J. Chem. Soc., Chem. Commun.* **1984**, 645. b) R. Isnin, C. Salam, A. E. Kaifer, *J. Org. Chem.* **1991**, *56*, 35. c) J. Liu, J. Alvarez, W. Ong, E. Román, A. E. Kaifer, *J. Am. Chem. Soc.* **2001**, *123*, 11148. d) B. González, I. Cuadrado, B. Alonso, C. M. Casado, M. Morán, A. E. Kaifer, *Organometallics* **2002**, *21*, 3544.

5 N. Kihara, M. Hashimoto, T. Takata, *Org. Lett.* **2004**, *6*, 1693.

6 a) M. Horie, Y. Suzaki, K. Osakada, *J. Am. Chem. Soc.* **2004**, *126*, 3684. b) M. Horie, Y. Suzaki, K. Osakada, *Inorg. Chem.* **2005**, *44*, 5844.

7 a) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem.—Eur. J.* **1996**, *2*, 709. b) H. Kawasaki, N. Kihara, T. Takata, *Chem. Lett.* **1999**, 1015.

8 Formation of rotaxane via metathesis of symmetrical olefins: a) J. S. Hannam, T. J. Kidd, D. A. Leigh, A. J. Wilson, *Org. Lett.* **2003**, *5*, 1907. b) A. F. M. Kilbinger, S. J. Cantrill, A. W. Waltman, M. W. Day, R. H. Grubbs, *Angew. Chem., Int. Ed.* **2003**, *42*, 3281.

9 a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18. b) R. H. Grubbs, T. M. Trnka, M. S. Sanfoed, in *Transition Metal-Carbene Complexes in Olefin Metathesis and Related Reactions*, ed. by A. Yamamoto, H. Kurosawa, Current Methods in Inorganic Chemistry, **2002**, Vol. 3, Chap. 4.

10 X.-Z. Zhu, C.-F. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 13158.

11 Crystal data for **2b**: $C_{44}H_{54}F_6FeNO_8P$, fw $= 925.72$, monoclinic, space group $P2_1/a$ (No. 14), $a = 38.521(4)$ Å, $b = 10.253(2)$ Å, $c = 11.378(1)$ Å, $\beta = 96.222(8)^\circ$, $V = 4467(1)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.376\,\mathrm{g\,cm^{-3}}$, No. of unique reflections $= 3536$ ($I > 3\sigma(I)$), $R = 0.058$, $R_w = 0.091$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-292617. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

12 **1a** (52 mg, 0.1 mmol) was dissolved in 2 mL of CH_2Cl_2 containing DB24C8 (54 mg, 0.12 mmol) followed by addition of 3,5-dimethylphenyl acrylate (35 mg, 0.2 mmol) and Ru catalyst (4.2 mg, 5×10^{-3} mmol). The mixture was refluxed for 15 h and solvent was removed by evaporation to form brown oil. The reprecipitation of crude product from CH_2Cl_2/Et_2O (2.5 mL/30 mL) gave brown solid which was collected, washed with Et_2O (10 mL × 2) and dried under reduced pressure to give **3** (80 mg, 0.072 mmol, 72%).

13 Data for **3**: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 2.29 (s, 6H, Me), 2.73 (br, 2H, $CH_2CH{=}CH$), 3.41–3.85 (16H, CH_2-DB24C8), 4.01–4.50 (21H, NCH_2, C_5H_5, C_5H_4, OCH_2-Axis, CH_2-DB24C8), 4.60 (br, 2H, NCH_2), 6.13 (d, 1H, C(=O)CH, $J = 15$ Hz), 6.70–6.72 (4H, C_6H_4-Axis, C_6H_3), 6.85 (s, 1H, C_6H_3), 6.88–6.97 (8H, C_6H_4-DB24C8), 7.23 (1H, CH_2CH), 7.34 (br, 2H, C_6H_4-Axis), 7.35 (br, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 21.3 (Me), 32.1 ($CHCH_2$), 47.7 (NCH_2), 51.6 (NCH_2), 65.9 (OCH_2), 68.5 (CH_2-DB24C8), 68.8 (C_5H_5), 69.4 (C_5H_4), 69.7 (C_5H_4), 70.3 (CH_2-DB24C8), 70.8 (CH_2-DB24C8), 113.0, 114.5, 119.1, 121.8, 122.7, 124.4, 127.4, 131.0, 139.1, 147.0, 147.6, 150.5, 159.0, 164.8 (C=O). C_5H_4-ipso is not observed due to the low intensity. IR (KBr): ν 3162 (N–H), 3073 (N–H), 1734 (C=O), 841 (P–F), 558 (P–F) $\mathrm{cm^{-1}}$. ESIMS: Anal. Calcd for $C_{55}H_{66}O_{11}NFe$: 972.4 Found: $m/z = 972.5$ $[M - PF_6]^+$. For NMR spectra of the rotaxanes, see Supporting Information.

14 A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783.

15 J. Kuwabara, D. Takeuchi, K. Osakada, *Organometallics* **2005**, *24*, 2705.