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Synthesis of macrocyclic polyethers via Ru complex-catalyzed metathesis cyclization and their use as the ring component of rotaxanes

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Abstract

Ring closing metathesis of the vinyl group-terminated oligoethers catalyzed by $RuCl_2(=CHPh)(PCy_3)_2$ yielded macrocyclic polyethers containing vinylene group. The ^1H and ^{13}C NMR spectra indicated the presence of C=C double bond (*trans*/*cis* = ca. 80:20). The obtained 23-membered cyclic ether reacted with benzyl(anthrylmethl)ammonium hexafluorophosphate to produce the pseudo-rotaxane as colorless crystals. X-ray crystallography revealed N–H···O hydrogen bonds and stacking of the aromatic planes between the host and guest molecules, which stabilized the rotaxane structure in the solid state. The ^1H NMR spectra of the solutions containing the macrocyclic polyether and several secondary ammonium salts indicated the formation of pseudo-[2]-rotaxanes.

Keywords: Ru-carbene complex; Ring-closing metathesis; Macrocycle; Rotaxane; Polyether; Metathesis; Ruthenium complex; Si-compound

1. Introduction

Rotaxanes [1] have attracted recent attention because of the unique structure that is composed of interlocked cyclic and linear molecules components and because of possible application to the molecular materials such as molecular machines [2], switching devices [3], and so on. There have been a number of reports of the rotaxanes and pseudorotaxanes containing crown ethers as the cyclic component and secondary ammonium salts as the axis component. Dibenzo[24]crown-8 (DB24C8) has the cavity size that is suited to form stable pseudo-rotaxanes with the secondary ammonium cations. The crown ethers composed of the –C–C–O– units, having other ring sizes such as dibenzo [18]crown-6 (DB18C6), dibenzo[30]crown-10 (DB30C10), dinaphtho[38]crown-10 (DN38C10) and dinaphtho[30] crown-10 (DN30C10), form the pseudo-rotaxanes with smaller association constants [4].

Recent progress of the ring-closing metathesis reaction [5] enabled formation of molecules with large size ring as well as direct synthesis of the interlocked molecules such as catenanes and rotaxanes [6–8]. Metathesis of the Cu(I) complexes with the phenanthroline ligands containing the two terminating vinyl groups was found to produce the catenane via selective coupling of the pairs of vinyl groups efficiently [7]. Very recently, Grubbs succeeded new synthesis of the rotaxane formed by the crown ether and the secondary ammonium cation with bulky terminal groups via repeated ring-opening and ring closing metathesis reaction of the polyether catalyzed by Ru complex [8].

In this paper, we report preparation of macrocyclic polyethers containing a C=C bond via the ring-closing metathesis [9] and its complexation with the secondary ammonium cations leading to the pseudo-rotaxanes as well as results of structure determination of the new pseudo-rotaxanes by X-ray crystallography.

2. Results and discussion

Acyclic oligoethers **1a** and **1b** undergo ring-closing metathesis reaction in the presence of catalytic amount of $RuCl_2(=CHPh)(PCy_3)_2$ at room temperature to produce

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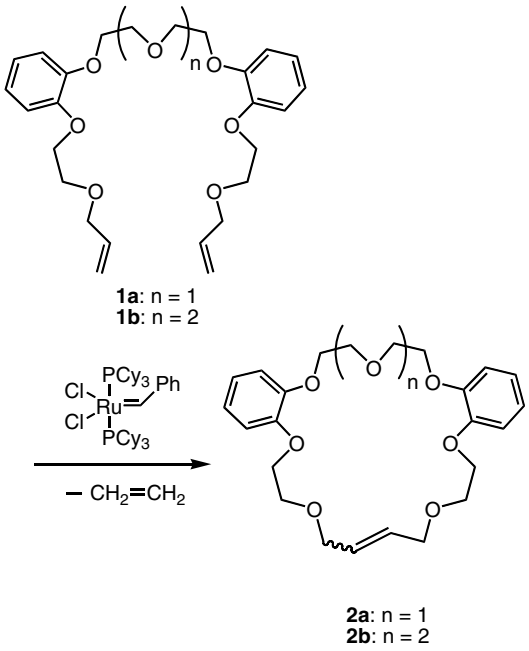
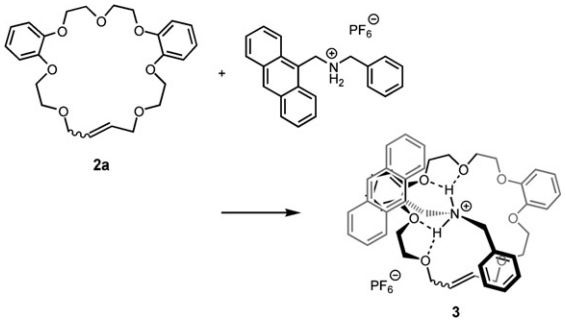
the 23-membered macrocyclic polyether **2a** and 26-membered polyether **2b** in the respective yields 91% and 58%, as shown in Eq. (1). The reactions were carried out in



(1)

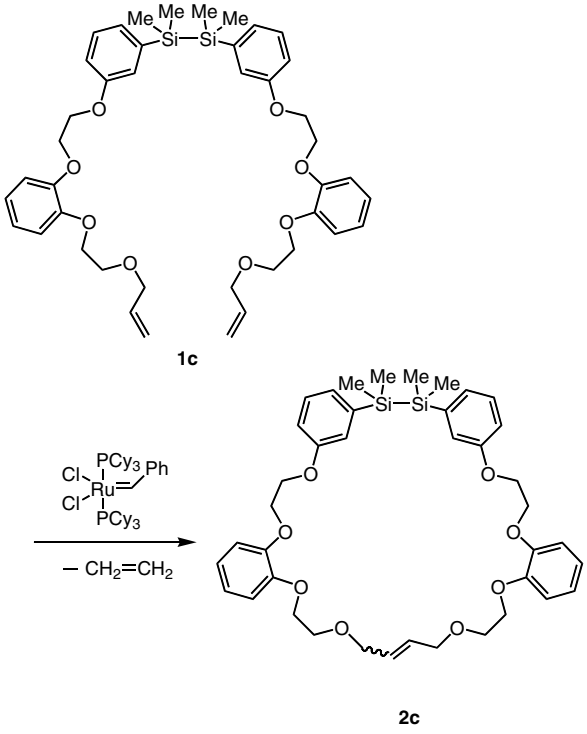
low concentration of the substrates (10 mM) in order to suppress the intermolecular metathesis of the vinyl groups to form their oligomers or polymers. These cyclic polyethers were isolated as white solids by recrystallization of the products from MeOH and characterized by NMR spectroscopy. The ^{1}H NMR spectra show two signals due to vinylic hydrogens with different peak areas, indicating that the macrocyclic polyethers contains the C=C double bond as a mixture of *trans* and *cis* isomers (**2a**: 89:11; **2b**: 87:13). Analogous cyclization of the disilane-containing polyether terminated by two vinyl groups, **1c**, led to the corresponding 32-membered macrocycle **2c**, as shown in Eq. (2). The cyclization occurs more slowly than the reaction in Eq. (1). The compound **1c** was converted into 50% after 2.5 h and gave the product **2c** in the isolated yield of 31% (*trans*:*cis* = 84:16).

Addition of a solution of anthrylmethy(benzyl)ammonium hexafluorophosphate in $CDCl_3/CD_3CN$ (60:40, vol/vol) to a solution of excess **2a** causes separation of the pseudo-rotaxane, **3**, composed of the cyclic polyether and the ammonium cation as shown in Eq. (3). Colorless crystals of **3** were grown selectively from the reaction



(3)

mixture that should contain an equilibrated mixture of **2a**, ammonium, and **3**. Fig. 1a depicts the structure of **3** determined by X-ray crystallography. The nitrogen atom of the cation is surrounded by the four oxygen atoms of the polyether. Fig. 1b displays interaction between the cyclic molecule



(2)

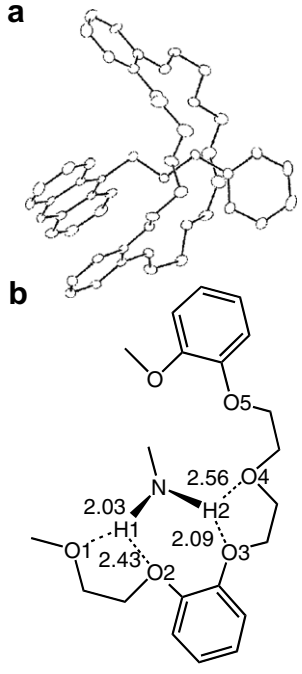


Fig. 1. (a) ORTEP drawing of rotaxane **3** determined by X-ray crystallography. (b) Distance between O and HN groups.

and dialkyl ammonium group. The distances between the four oxygen atoms and the nitrogen of the host and guest are in the range, 2.97–3.21 Å. Calculation of the hydrogen positions of attached to the nitrogen atom by assuming the ideal geometry ($d = 0.97$ Å) also indicated close contact of the hydrogen atoms with oxygen atoms of the polyether (N–H–O = 2.0–2.6 Å). The four oxygen atoms form the plane which contains the NH_2 group of the guest molecule. The distance between the anthryl group of the axis and the phenylene ring of the macrocycle is 3.4 Å, indicating the π–π stacking interaction of the host and guest. These aromatic planes are parallel from each other, similarly to the previously reported rotaxanes of crown ethers with the secondary ammonium cation [4,10]. The stacking serves to stabilize the pseudo-rotaxane formation.

The crystal structure indicates that the C=C bond of the cyclic polyether has *trans* configuration in the crystal structure of rotaxane, although the starting cyclic compound is a mixture of the *trans* and *cis* isomers. Dissolution of once isolated the rotaxane **3** in CD_3CN shows the presence of the rotaxane in 22% and **2a** and the ammonium salt in 78%. The NMR spectra show the presence of *trans* and *cis* C=C double bond in the macrocyclic polyether in the mixture. These results are explained by the results that the pseudorotaxane contains both the cyclic polyether with *trans* and *cis* C=C double bonds and that the pseudorotaxane with *trans*-C=C double bond forms single crystals more easily than that with *cis*-C=C bond (see Fig. 2).

Reaction of the macrocyclic ethers **2a** and **2b** with various ammonium salts form the rotaxanes although isolation of the rotaxanes was not feasible. Formation of the rotaxanes is confirmed by the ^1H NMR spectra which show the signal at lower field positions. The ^1H NMR spectrum of dibenzylammonium hexafluorophosphate shows the CH_2N hydrogen signal at δ 4.18, while the spectrum of a mixture of the ammonium salt with **2b** shows not only the signal at that position but also that at δ 4.57. The latter signal is assigned to the CH hydrogens of the pseudorotaxanes formed in the solution. (4-*t*-Butylbenzyl)hexylammonium hexafluorophosphate whose cationic part is unsymmetrical shows two signals due to CH_2 hydrogens at δ 4.12 and 2.98. Both signals are shifted to lower magnetic positions. Table 1 summarizes the results of the complexation and includes the NMR peak positions before and after complexation as well as the equilibrium constants of the axes with the crown ether **2b** [13]. The ammonium salts having one bulky aromatic group and one benzyl group shows relatively high association constants. The two aromatic groups may enhance the pseudo-rotaxane formation, presumably via the π–π stacking interaction. The association constant of dibenzylammonium hexafluorophosphate is lower than those of anthrylmethy(benzyl)ammonium hexafluorophosphate and (4-*t*-butylbenzyl)phenylammonium hexafluorophosphate, although it has two phenyl group. The presence of bulky groups such as anthryl group and 4-*t*-butylphenyl group may serve to block the dissociation of the macrocycle.

In summary, the metathesis reaction using Ru complex-catalyzed ring closing metathesis of the vinyl group-terminated polyethers produce the macrocyclic polyethers with vinylene groups in 23 to 32-membered ring-size. One of the cyclic polyethers forms rotaxanes

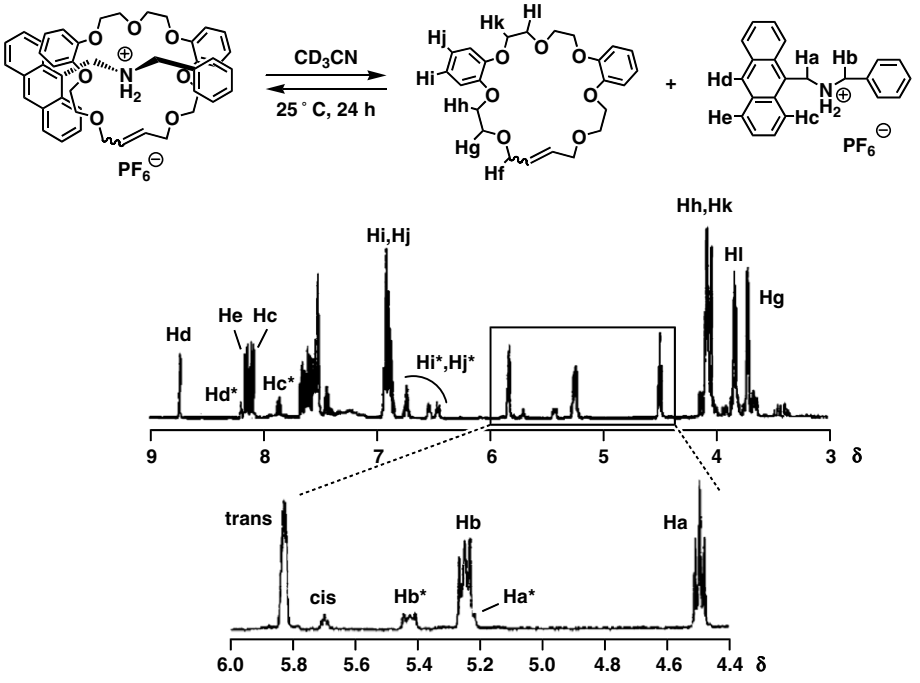
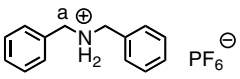
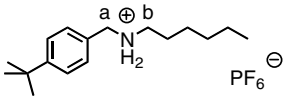
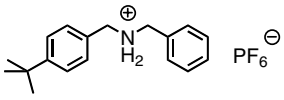
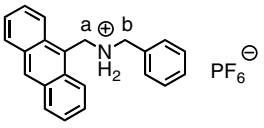
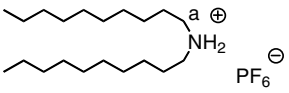
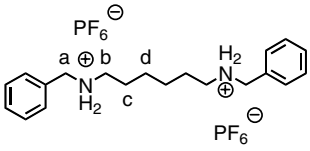


Fig. 2. ^1H NMR spectrum (400 MHz) of a CD_3CN solution of **3**. Assignment of the peaks is shown in the chemical formula. The peak with asterisk is assigned to the rotaxane, and the peak without asterisk is assigned to dissociated cyclic and linear molecules.

Table 1
Formation of pseudo-rotaxanes

Axes	^{1}H NMR[a]		K_{app}[b] (M^{-1})
	Axe	Rotaxane	
	a 4.18 (t)	4.57 (t)	61
	a 3.12 (t) b 2.98 (m)	4.26 (m) 2.34 (m)	83
	4.20 (t) 4.18 (t)	4.61 (t) 4.49 (t)	190
	a 5.20 (t) b 4.44 (t)	5.45 (t) 5.26 (t)	270
	a 2.95 (m)	3.19 (m)	42
	a 4.18 (t) b 3.30 (m) c 1.70 d 1.40	4.43 (br) 3.14 (br), 3.29 (br) 1.47 (br) 1.10 (br)	64

NMR data and apparent association constants.
[a] Measured at 25 °C in $CDCl_3/CD_3CN$ (60:40).
[b] K_{app} (M^{-1}) = [pseudorotaxanes][**2a**]$^{-1}$[axe]$^{-1}$.

with the ammonium hexafluorophosphates having various substituents at the nitrogen. ^{1}H NMR study revealed the looser host–guest binding than the ideal complexation of crown ethers.

3. Experimental

3.1. General, measurement, materials

All operations were carried out under dry nitrogen or argon atmosphere unless stated otherwise. Column chromatography was performed using silica gel 60 N (spherical, neutral, mesh 100–210) from Kanto Chemicals. Diethylene glycol bis(2-hydroxyphenyl) ether was synthesized from 2-benzyloxyphenol and diethylene glycol bis(*p*-tosylate) according to the similar procedure reported previously [11]. Ethylene glycol (2-(2-allyloxyethoxy)phenyl) ether was synthesized similarly from 2-(2-hydroxyethoxy)phenol and ethylene glycol allyl ether *p*-tosylate. ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{29}Si{^{1}H} NMR spectra were taken on a Varian Mercury-300 or JEOL GX-400 spectrometer. Chemical shifts were referenced with the solvent peaks.

3.2. Ethylene glycol allyl ether p-tosylate

Ethylene glycol allyl ether *p*-tosylate was synthesized by the modification of the reported procedure [12].

A solution of ethylene glycol monoallyl ether (18.3 g, 180 mmol) in THF (98 ml) was added to a 4.6 M aqueous NaOH solution at 0 °C. A THF solution (80 ml) of *p*-toluenesulfonyl chloride (35.6 g, 188 mmol) was added dropwise over a period of 4 h at 0–5 °C and stirred for 3 h at

the temperature. The reaction mixture was poured onto an ice-water (30 ml) and extracted with CH_2Cl_2 (160 ml). The organic phase was washed with water (120 ml × 2), and dried over Na_2SO_4. The solvent was removed in vacuo to afford the product as a clear oil by shaking vigorously with hexane to remove unreacted *p*-toluenesulfonyl chloride (38.2 g, 83%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.78 (2H, d, *J* 8.4, C_6H_4), 7.32 (2H, d, *J* 8.4, C_6H_4), 5.86–5.73 (1H, m, CH_2=C*H*–), 5.23–5.11 (2H, m, CH_2=CH–), 4.15 (2H, t, $J = 4.7$, OCH_2CH_2OTs), 3.92 (2H, d, *J* 5.5, CH_2=CH–CH_2), 3.60 (2H, t, $J = 4.9$ and 4.4, OCH_2CH_2OTs), 2.42 (3H, s, CH_3). ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): δ_C 144.76 (C_6H_4), 134.04 (allyl), 132.98 (C_6H_4), 129.76 (C_6H_4), 127.93 (C_6H_4), 117.36 (allyl), 72.10 (OCH_2), 69.19 (OCH_2), 67.38 (OCH_2), 21.57 (CH_3).

Ethylene glycol (2-(2-allyloxyethoxy)phenyl) ether *p*-tosylate was synthesized similarly by the tosylation of ethylene glycol (2-(2-allyloxyethoxy)phenyl) ether.

3.3. 1,2-Bis(3-methoxymethoxyphenyl) 1,1,2,2-tetramethyldisilane

To a dry THF solution of 3-methoxymethoxyphenyl magnesium bromide, formed in situ by adding a dry THF solution (6 mL) of 3-methoxymethoxyphenyl bromide (2.00 g, 9.2 mmol) to magnesium (0.243 g, 10 mmol) in dry THF (2 mL), was added dropwise a THF solution (6 mL) of 1,2-dichloro-1,1,2,2-tetramthyldisilane (0.842 g, 4.5 mmol) over a period of 1 h at room temperature, and the reaction mixture was stirred at room temperature for 18 h and at 50 °C for 7 h. NH_4Cl aq. (20 mL) was added to the reaction mixture and the organic fraction was extracted with ether (40 ml × 3), which was washed with brine (40 ml × 3) and dried over Na_2SO_4. The volatiles were removed in vacuo and the residue was purified by SiO_2 column chromatography hexane:acetone = 5:1 as eluent to give 1,2-bis(3-methoxymethoxyphenyl) 1,1,2,2-tetramethyldisilane as yellow oil (0.78 g, 2.0 mmol, 44%). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.29–6.98 (8H, m, C_6H_4), 5.13 (4H, s, OCH_2O), 3.46 (6H, s, OCH_3), 0.34 (12H, s, $SiCH_3$). ^{29}Si{^{1}H} NMR (79 MHz; $CDCl_3$): δ −21.3.

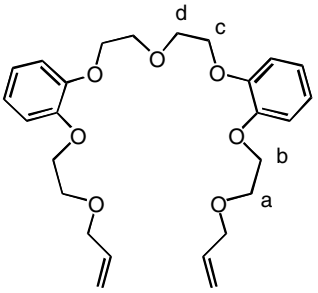
3.4. 1,2-Bis(3-hydroxyphenyl) 1,1,2,2-tetramethyldisilane

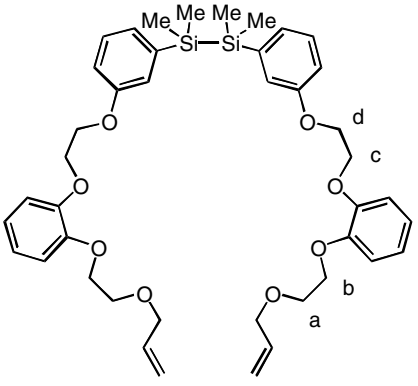
MeOH (33 mL) and HCl aq. (1 N, 5.25 mL) were added to 1,2-bis(3-methoxymethoxyphenyl) 1,1,2,2-tetramethyldisilane (1.56 g, 3.99 mmol) and the mixture was stirred at 45 °C for 2.5 h. Brine (20 mL) was added to the reaction mixture and the organic fraction was extracted with ether (20 mL × 3), which was dried over Na_2SO_4. The volatiles were removed in vacuo and the residue was purified by SiO_2 column chromatography hexane:acetone = 5:1 as eluent to give 1,2-bis(3-hydroxyphenyl) 1,1,2,2-tetramethyldisilane (1.02 g, 3.37 mmol, 85%). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.26–6.80 (8H, m, C_6H_4), 6.00 (2H, br, OH), 0.29 (12H, s, $SiCH_3$).

3.5. Diethylene glycol bis(2-(2-allyloxyethoxy)phenyl) ether (**1a**)

To a dry MeCN (50 ml) suspension of K_2CO_3 (2.88 g, 20.7 mmol) was added diethylene glycol bis(2-hydroxyphenyl)ether (1.99 g, 6.87 mmol) and stirred vigorously at 85–90 °C for 30 min. After addition of a dry MeCN (32 ml) solution of ethylene glycol allyl ether *p*-tosylate (3.54 g, 13.8 mmol) over a period of 30 min, the mixture was refluxed for 18 h. The MeCN soluble part was separated and the residue was extracted with ethyl acetate (30 ml) and then with CH_2Cl_2 (30 ml). After the solvents were evaporated, the residue was dissolved in CH_2Cl_2 (50 ml), washed with 1 M aqueous NaOH solution (50 ml) and then with water (50 ml) and dried over $MgSO_4$. The solvent was evaporated to give a yellow oil, which was purified by SiO_2 column chromatography hexane: acetone = 1:1 as eluent to give **1a** (2.80 g, 89%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.02–6.88 (8H, m, 2 × C_6H_4), 5.95 (2H, m, C*H*=CH_2), 5.32 (2H, dd, CH=CH_2), 5.20 (2H, dd, CH=CH_2), 4.21 (8H, m, H_b and H_c), 4.12 (4H, d, CH_2=CH–CH_2), 3.98 (4H, t, H_d), 3.83 (4H, t, H_a).

Compounds **1b** was prepared analogously. Compounds **1c** was prepared from ethylene glycol (2-(2-allyloxyethoxy)phenyl) ether *p*-tosylate and 1,2-bis(3-hydroxyphenyl) 1,1,2,2-tetramethyldisilane by the similar procedure. **1b**: ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.97–6.85 (8H, m, 4 × C_6H_4), 5.93 (2H, m, C*H*=CH_2), 5.31 (2H, dd, CH=CH_2), 5.18 (2H, dd, CH=CH_2), 4.17 (8H, t, 4 × OCH_2), 4.09 (4H, d, CH_2=CH–CH_2), 3.87 (4H, t, 2 × OCH_2), 3.80 (4H, t, 2 × OCH_2), 3.75 (4H, s, 2 × OCH_2). **1c**: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.06–6.80 (16H, m, 4 × C_6H_4), 5.89 (2H, m, C*H*=CH_2), 5.27 (2H, dd, CH=CH_2), 5.14 (2H, dd, CH=CH_2), 4.35 (8H, t, H_b and H_c), 4.17 (4H, t, H_d), 4.06 (4H, d, CH_2=CH–CH_2), 3.80 (4H, t, H_a), 0.34 (12H, s, Me). ^{29}Si{^{1}H} NMR (79 MHz; $CDCl_3$): δ −21.3.

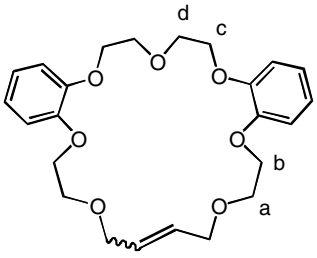


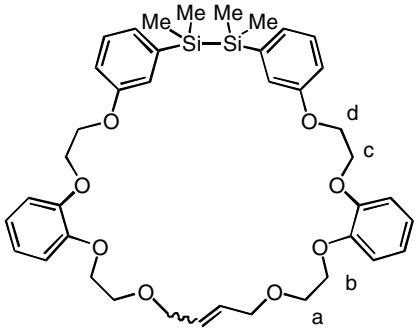


3.6. Cyclic compound **2a**–**2c**

$Cl_2(PCy_3)_2Ru{=}CHPh$ (9.0 mg, 0.011 mmol) was added to a solution of diethylene glycol bis[2-(2-allyloxyethoxy)phenyl]ether (199 mg, 0.434 mmol) in dry dichloromethane (20 ml) and the solution stirred at 40 °C for 3 h. The solvent was removed in vacuo and the residue was subjected to column chromatography (CH_2Cl_2:EtOAc = 1:1 (v/v) as eluent) to yield **2a** as a white, crystalline solid (150 mg, 81%). ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.93–6.88 (8H, m, $2\times C_6H_4$), 5.89 (1.6H, m, CH=CH (*trans*)), 5.77 (0.4H, m, CH=CH (*cis*)), 4.27 (0.8H, d, J 4.8, CH=CHCH_2 (*cis*)), 4.17 (11.2H, m, CH=CHCH_2 (*trans*), H_b, and H_c), 4.00 (4H, t, H_d), 3.84 (4H, t, H_a). ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): δ 149.40, 148.93, 141.06, 129.34, 121.93, 121.42, 115.90, 114.00, 71.17, 70.36, 69.89, 69.05, 68.33.

Compounds **2b** and **2c** were prepared analogously. **2c**: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.01–6.80 (16H, m, $4\times C_6H_4$), 5.77 (1.6H, m, CH=CH (*trans*)), 5.70 (0.4H, m, CH=CH (*cis*)), 4.32 (4H, t, H_d), 4.20 (4H, t, H_c), 4.14 (4.8H, m, CH=CHCH_2 (*cis*) and H_b), 4.05 (3.2H, d, CH=CHCH_2 (*trans*)), 3.77 (4H, t, H_a), 0.33 (12H, s, Me), ^{29}Si{^{1}H} NMR (79 MHz; $CDCl_3$): δ −21.4.





3.7. X-ray crystallography

Crystals of **3** suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2-hexane and mounted in glass capillary tubes under argon. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation ($\lambda = 0.71069$ Å) and ω-2θ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out by using a program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and these locations were included in the structure calculation without further refinement of the parameters. $C_{46}H_{50}O_7NPF_6$, $0.5\times0.38\times0.35$ mm, $M_r = 873.87$, monoclinic, $P2_1/c$ (No. 14), $a = 11.180(2)$, $b = 26.429(6)$, $c = 14.842(5)$ Å, $\beta = 106.64(5)°$, $V = 4297$ Å^3, $Z = 4$, $D_c = 1.351$ g cm^{-1}, $\mu = 1.42$ mm^{-1}, $F(000) = 1832$, graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by full-matrix least-squares technique to $R = 0.087$, $R_w = 0.080$ using 3080 reflections with $F_o > 3\sigma(F_o)$.

4. Supplementary material

CCDC 612398 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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