(Mesitylene)ruthenium π-complexes with benzo-15-crown-5 and dibenzo-18-crown-6

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ABSTRACT

The reactions of benzo-15-crown-5 and dibenzo-18-crown-6 with 1 equiv. of $[(mes)Ru(MeNO_2)_3]^{2+}$ (mes = $1,3,5-C_6H_3Me_3$) give the mononuclear complexes $[(mes)Ru(\eta^6-benzo-15-crown-5)]^{2+}$ (**1**) and $[(mes)Ru(\eta^6-dibenzo-18-crown-6)]^{2+}$ (**2**) in 50% yield. Similar reaction with 2 equiv. of $[(mes)Ru(MeNO_2)_3]^{2+}$ produces the dinuclear complex $[(\mu-\eta^6:\eta^6-dibenzo-18-crown-6)Ru_2(mes)_2]^{4+}$ (**3**) in 96% yield as a 2:3 mixture of *cis*- and *trans*-isomers. Structures of **2**(OTf)$_2$ and *trans*-**3**(OTf)$_4$ were confirmed by X-ray diffraction. The NMR titration showed that mononuclear dications **1** and **2** bind Na$^+$ ion less effective (K_a = 600 and 250 M^{-1}) than free benzo-15-crown-5 and dibenzo-18-crown-6 (K_a = 2 × 10^5 and 5 × 10^6 M^{-1}). The dinuclear tetracation **3** does not bind Na$^+$ within measurable limits of NMR titration method. The electrochemical behaviour of complexes **1**–**3** was studied in propylene carbonate solution. They exhibit a partially chemically reversible Ru(II)/Ru(I) reduction, which in the case of the dinuclear complex **3** proceeds through two slightly separated steps. The redox activity of the complexes is substantially unaffected by the presence of sodium ion.

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1. Introduction

Despite fundamental importance and numerous industrial applications of benzocrown ethers [1], their transition metal π-complexes are still rare and represented mainly by chromium and ruthenium compounds. For instance, Cr(CO)$_3$ derivatives were used for selective functionalization of dibenzocrown ethers [2] and IR-detection of sodium ion and aromatic molecules [3]. The ruthenium complex $[CpRu(\eta^6-benzo-15-crown-5)]^+$ was employed in alkali metal intercalation with metal thiophosphates [4]. Complexes of benzocrown ethers with the Ru$_6$C(CO)$_{14}$ cluster unit were immobilized on aminated polymers to obtain hydrogenation catalysts [5], while compounds $[(\eta^6-benzocrown)RuCl_2]_2$ were suggested for biphasic catalysis [6].

However, in most of the previous studies the influence of transition metal on receptor ability of the crown ether moiety was not investigated. Recently, we have demonstrated that π-coordination of the $[(C_4Me_4)Co]^+$ fragment with benzocrown ethers significantly decreases their Na$^+$ binding ability [7]. Herein we report the synthesis of (mesitylene)ruthenium π-complexes with benzo-15-crown-5 and dibenzo-18-crown-6 along with their structural, NMR titration, and electrochemical studies.

## 2. Results and discussion

2.1. Synthesis

The reactions of benzo-15-crown-5 and dibenzo-18-crown-6 with 1 equiv. of the solvate dication $[(mes)Ru(MeNO_2)_3]^{2+}$ (mes = $1,3,5-C_6H_3Me_3$), generated from $[(mes)RuCl_2]_2$ and AgOTf in nitromethane, give the mononuclear complexes $[(mes)Ru(\eta^6-benzo-15-crown-5)]^{2+}$ (**1**) and $[(mes)Ru(\eta^6-dibenzo-18-crown-6)]^{2+}$ (**2**) in ca. 50% yield (Scheme 1). An alternative synthesis by direct reaction of $[(mes)RuCl_2]_2$ with the benzocrown ethers in refluxing CF$_3$COOH [8] failed because of their fast decomposition under these conditions.

Interestingly, the reaction of dibenzo-18-crown-6 with 2 equiv. of $[(mes)Ru(MeNO_2)_3]^{2+}$ gives the dinuclear complex $[(\mu-\eta^6:\eta^6-dibenzo-18-crown-6)Ru_2(mes)_2]^{4+}$ (**3**) in 96% yield as a mixture of *cis*- and *trans*-isomers in 2:3 ratio according to ^{1}H NMR (Scheme 2).[1] The isomers can be partially separated by fractional crystallization due to the better solubility of the *trans*-**3**(OTf)$_4$ in acetone. This
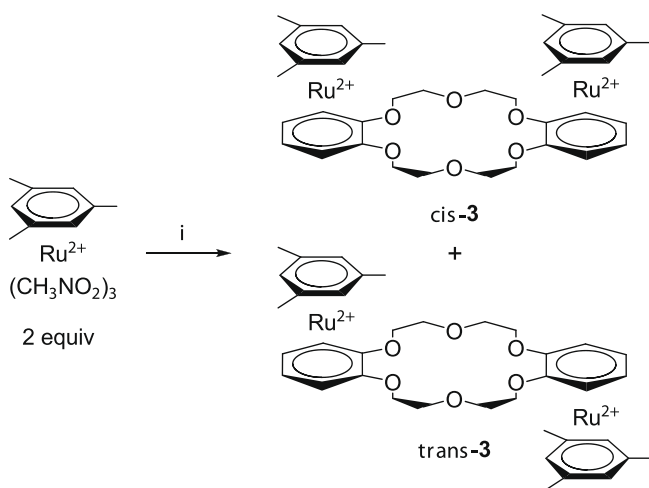
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[1] After X-ray diffraction analysis the crystals of *trans*-**3**(OTf)$_4$ were dissolved in CD$_3$NO$_2$ and ^{1}H NMR spectrum was measured. This allowed to assign the signals of *trans*-**3** isomer and consequently those of *cis*-**3**. The ^{1}H NMR spectra of partially separated *cis*- and *trans*-isomers of **3**(OTf)$_4$ are given in supplementary material.

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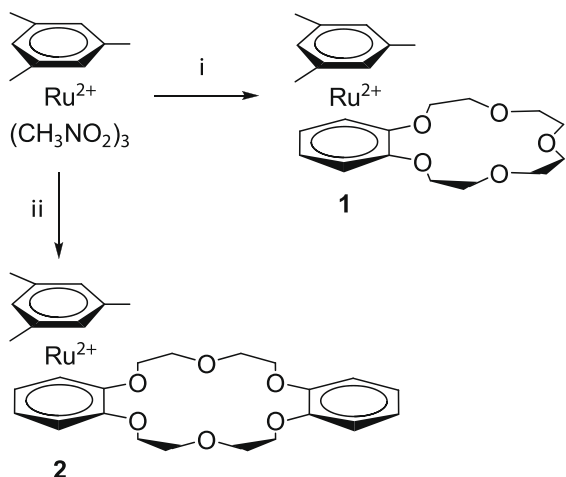
Scheme 1. Synthesis of mononuclear complexes **1** and **2**: (i) benzo-15-crown-5 and (ii) dibenzo-18-crown-6.
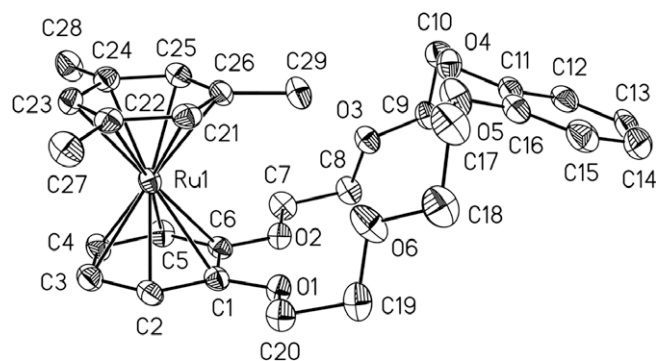

Fig. 1. Structure of dication **2**. Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å): Ru1–C1 2.303(3), Ru1–C2 2.230(3), Ru1–C3 2.208(3), Ru1–C4 2.213(3), Ru1–C5 2.246(3), Ru1–C6 2.312(3), Ru1–C21 2.222(3), Ru1–C22 2.246(3), Ru1–C23 2.219(3), Ru1–C24 2.225(3), Ru1–C25 2.220(3), Ru1–C26 2.243(3).
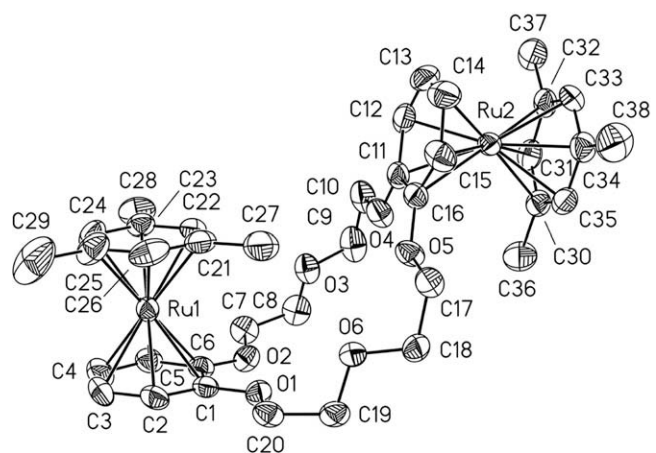

Scheme 2. Synthesis of tetracationic complex **4**: (i) dibenzo-18-crown-6.

Fig. 2. Structure of tetracation *trans*-**3**. Atoms are represented by 40% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å): Ru1–C1 2.299(4), Ru1–C2 2.226(5), Ru1–C3 2.211(5), Ru1–C4 2.203(5), Ru1–C5 2.207(5), Ru1–C6 2.278(5), Ru1–C21 2.233(5), Ru1–C22 2.219(5), Ru1–C23 2.252(4), Ru1–C24 2.204(5), Ru1–C25 2.213(5), Ru1–C26 2.190(6), Ru2–C11 2.306(5), Ru2–C12 2.211(5), Ru2–C13 2.189(5), Ru2–C14 2.189(5), Ru2–C15 2.219(5), Ru2–C16 2.302(4), Ru2–C30 2.224(4), Ru2–C31 2.203(5), Ru2–C32 2.219(5), Ru2–C33 2.198(5), Ru2–C34 2.217(5), Ru2–C35 2.208(5).

allowed us to grow up a single crystal of *trans*-**3**(OTf)$_4$ for X-ray diffraction analysis.

2.2. Structures of **2** and trans-**3**

The structures of compounds **2**(OTf)$_2$ and *trans*-**3**(OTf)$_4$ were determined by X-ray diffraction (Figs. 1 and 2). In the dication **2** the distance from the ruthenium atom to the mesitylene ring plane (1.718 Å) is notably shorter than that to the crown ether benzene ring (1.748 Å). The six-membered rings are almost parallel (dihedral angle 1.4°) and arranged in the staggered conformation (torsion angle 22.4°). Due to interaction with the metal atom, the perimeter of the coordinated benzene ring of the crown ether (8.509 Å) is significantly larger than that of the non-coordinated one (8.358 Å). In general, geometric parameters of tetracation *trans*-**3** are similar to those of dication **2**. However, the crown ether moiety in *trans*-**3** displays more common boat-type conformation with approximately orthogonal benzene rings (100.5°) unlike ladder-type conformation in **2**.

Interestingly, the ruthenium atoms in **2** and *trans*-**3** are non-symmetrically coordinated to the benzene rings of the crown ether being slipped by 0.08 Å away from the oxygen atoms. Accordingly, the distances from ruthenium to the substituted carbon atoms C1, C6, C11, and C16 (av. 2.308 Å for **2**, av. 2.296 Å for *trans*-**3**) are nota-

bly longer than other Ru–C bonds (av. 2.227 Å for **2**, av. 2.212 Å for *trans*-**3**). This slip distortion can be explained by conjugation of benzene ring with oxygen atoms, similar to that proposed for manganese and ruthenium catechol complexes [9]. The analysis of the Cambridge Structural Database revealed that the majority of transition metal complexes with *ortho*-C$_6$H$_4$(OR)$_2$ ligands display this type of non-symmetrical coordination.[2]

2.3. NMR titration

Ability of the benzocrown ether complexes **1**–**3** to bind sodium ions was estimated by ^{1}H NMR titration with Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] in CD$_3$NO$_2$. The typical spectral changes are shown in Fig. 3 for complex **2**, as a representative example. The signals of the CH$_2$ groups display the largest shifts upon Na$^+$ complexation, however the complicated splitting makes them useless for quanti-

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[2] CSD search (November 2008 update release, version 5.30) for compounds containing M(*ortho*-C$_6$H$_4$(OR)$_2$) fragment gives 77 unique non-disordered structures. In these structures M–C$_O$ distances were found to be statistically larger than M–C$_H$ for av. 0.056 Å (range –0.040 to 0.259 Å).
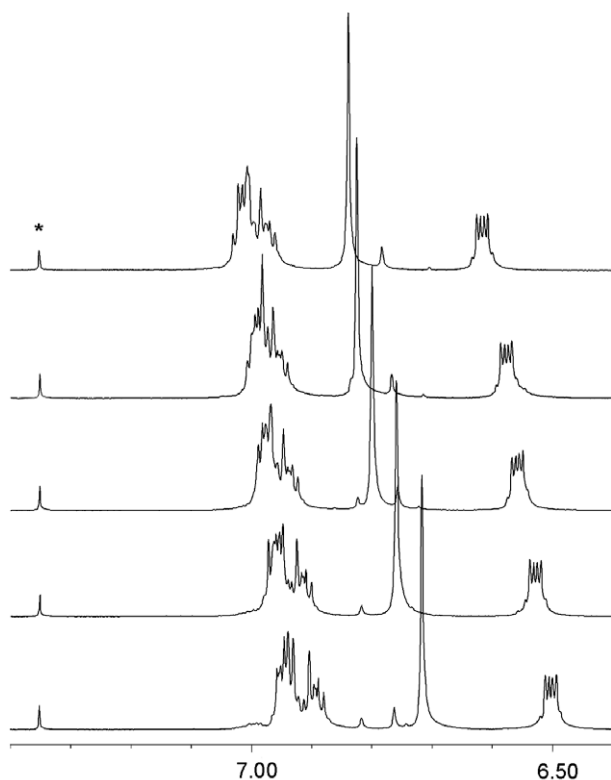
Fig. 4. Cyclic voltammetric responses recorded at a glassy-carbon electrode in PC solution of **2**(OTf)$_2$ (0.4×10^{-3} mol dm^{-3}). [NBu$_4$]PF$_6$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate: 0.2 V s^{-1}.

tative measurement of association constants (K_a). Therefore the signals of the coordinated aromatic ring of the benzocrown ether (namely, mean value of the multiplet at ca. 6.50 ppm) were used for this purpose. The determined K_a values for the mononuclear dications **1** (600 ± 100 M^{-1}) and **2** (250 ± 50 M^{-1}) are much smaller than those for the parent benzo-15-crown-5 and dibenzo-18-crown-6 ($K_a = 2 \times 10^5$ and 5×10^6 M^{-1}) [10]. The dinuclear tetracation **3** does not bind Na$^+$ within measurable limits of NMR titration method ($K_a < 1$ M^{-1}). These results indicate that π-coordination of the cationic [(mes)Ru]$^{2+}$ fragments decreases the sodium ion binding ability of the benzocrown ethers by several orders of magnitude, presumably due to electrostatic repulsion [7].

2.4. Electrochemistry

The electron transfer activity of the mononuclear dication **2** in propylene carbonate (PC) solution is illustrated in Fig. 4. The dication displays a substantially irreversible oxidation and two main subsequent reductions, only the first of which possesses features of partial chemical reversibility. An unresolved intermediate process at about −1.5 V is also present.

Since controlled potential coulometry of the first cathodic step ($E_w = 1.1$ V vs. SCE) did not afford satisfactory results (the electrolysis current was very time-consuming and unable to go at end probably because of slight electrode poisoning effects), the process has been reliably assigned as a one-electron step by comparison with the one-electron oxidation of an equimolar amount of the ferrocendiyl complex of comparable molecular weight [[bis(3,5-dimethylphenyl)phosphino]ethyl]-2-[2-[bis(3,5-dimethylphenyl)phosphino]phenyl]ferrocene (MW = 770.7; E_{pa} = +0.33 V; see Fig. S1 in Supplementary Material).

Such a process is therefore attributed to the Ru(II)/Ru(I) reduction ($E^{\circ\prime}$ = − 0.90 V vs. SCE). Analysis of the pertinent cyclic voltam-
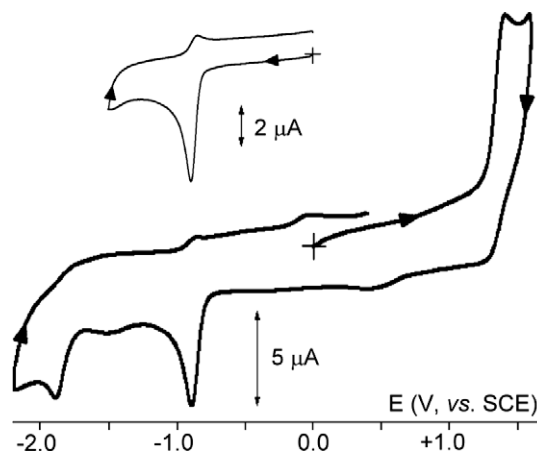
metric response with the scan rate progressively increasing from 0.02 V s^{-1} to 5.0 V s^{-1} confirms that the diffusion controlled process is coupled to fast chemical complications. In particular: (i) the current function $i_{pc} v^{-1/2}$ maintains substantially constant; (ii) the current ratio i_{pa}/i_{pc} progressively increases from 0.1 to 0.4 (which means that the Ru(I) congener is quite unstable); and (iii) the peak-to-peak separation does not depart significantly from the theoretical value of 57 mV expected for a reversible one-electron process [11].

As far as the second cathodic step is concerned (E_p = −1.93 V), even if it cannot be ruled out that it might arise from the Ru(I)/Ru(0) process, we are keen to assign it to the byproducts arising from the Ru(II)/Ru(I) process, in that the ratio between its peak height and that of the first reduction, which for instance is about 0.4 at 0.1 V s^{-1}, tends to increase with the scan rate. It is however noted that such ratio reaches the value of 0.6 even at the highest scan rate, in agreement with the impossibility to prevent the chemical complications accompanying the Ru(II)/Ru(I) process. On passing, we attribute also the cited intermediate reduction process at −1.5 V to a short lived byproduct. Finally, the anodic process (E_p = +1.38 V) is naively assigned to the Ru(II)/Ru(III) oxidation, the extent of chemical reversibility of which by analysis of the response with the scan rate was not determined because of its overlapping with the solvent discharge.

A substantially similar cathodic picture is displayed by complex **1**, the two main reductions of which occur at $E^{\circ\prime}$ = −0.89 V and E_p = −1.86 V, respectively. Unexpectedly no anodic process was detected.

Passing to the dinuclear tetracation **3**, its voltammetric fingerprint is illustrated in Fig. 5. As shown, the cathodic profile is reminiscent to that of the mononuclear complexes **1** and **2**, but in this case the first reduction is partially splitted into two separated processes (at about −0.8 V) possessing features of limited chemical reversibility. The intermediate process at about −1.5 V, which precedes the second main reduction (E_p = −1.97 V), is better resolved probably because the by-product arising from the first reduction processes is more long lived.

It is noted that in the present case the poisoning electrode effects were severe than those observed for the mononuclear complexes thus requiring cleaning of the electrode surface after each scan. Such effect prevented an accurate measurement of the number of electrons involved in the different processes. It does not seem however too ventured to assume that the one-electron reduction of the two Ru(II) centres are slightly separated, which could imply a slight interaction between the two ruthenium

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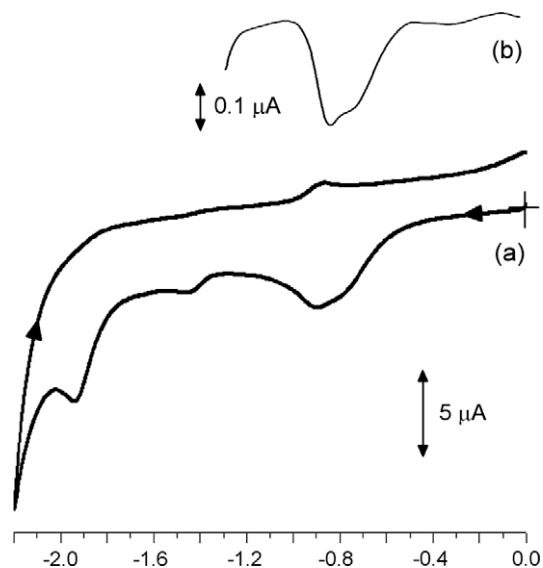**Fig. 3.** The ^{1}H NMR spectra of **2**(OTf)$_2$ (aromatic region) in the presence of 0.00, 0.20, 0.65, 0.99, and 5, 17 equiv. (from bottom to top) of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]. The unchanged signal of CHCl$_3$ is marked with asterisk.

Fig. 5. Cyclic (a) and differential pulse (b) voltammetric responses recorded at a glassy carbon electrode in PC solution of **3**(OTf)$_4$ (0.3×10^{-3} mol dm^{-3}). [NBu$_4$]PF$_6$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rates: (a) 0.2 V s^{-1}; (b) 0.02 V s^{-1}.

fragments [11]. No oxidation process was detected in the anodic window of the solvent.

As far as the affinity of the present complexes for the Na$^+$ ion is concerned, in agreement with the NMR titrations, essentially no variation in the redox profiles of the complexes was recorded upon the progressive addition of NaClO$_4$. In fact, the reduction processes were shifted towards less negative potential values by about 0.01 V.

3. Conclusion

Reactions of benzocrown ethers with the cationic [(mes)Ru]$^{2+}$ fragment afford mono and binuclear π-complexes **1–3**. Ruthenium complexation strongly decreases Na$^+$ binding ability of the crown ether cavity. The structures of cations **2** and **3**, as well as the analysis of Cambridge Crystallographic Database revealed that non-symmetrical coordination is typical for transition metal complexes with ortho-C$_6$H$_4$(OR)$_2$ ligands. Electrochemical studies shown that **1–3** exhibit partially chemically reversible Ru(II)/Ru(I) reductions, which are unaffected by the presence of Na$^+$ ions.

4. Experimental

4.1. General

All reactions were carried out under argon in anhydrous solvents which were purified and dried using standard procedures. The isolation of products was conducted in air. Benzo-15-crown-5 and dibenzo-18-crown-6 were purchased from Aldrich and used as received. [(mes)RuCl$_2$]$_2$ was prepared according to the literature procedure [12]. The ^{1}H NMR spectra were recorded in CD$_3$NO$_2$ with Bruker Avance-400 instrument. The chemical shifts are given in ppm relative to internal SiMe$_4$.

4.2. [(mes)Ru(η^6-benzo-15-crown-5)](CF$_3$SO$_3$)$_2$ (**1**(OTf)$_2$)

A mixture of [(mes)RuCl$_2$]$_2$ (58 mg, 0.1 mmol) and CF$_3$SO$_3$Ag (103 mg, 0.4 mmol) was stirred for 1 h in 5 ml of nitromethane. The color of the reaction mixture changed from brown to orange and precipitate of AgCl was centrifuged off. The centrifugate was

treated with benzo-15-crown-5 (94 mg, 0.35 mmol) and refluxed for 8 h (reaction at room temperature gives lower yields, ca. 30–40%). The resulting mixture was filtered and evaporated in vacuo. The residue was washed with CH$_2$Cl$_2$ (3 × 2 ml) to remove the excess of the crown ether. The solid obtained was dissolved in acetone and eluted through a short layer of Al$_2$O$_3$ (5 cm) by acetone/EtOH mixture (1:1). The filtrate was concentrated to ca. 2 ml and 20 ml of Et$_2$O was added giving white precipitate of **1**(OTf)$_2$ (103 mg, 53%).

^{1}H NMR: δ 2.57 (s, 9H, C$_6$H$_3$*Me$_3$*), 3.64 (m, 8H, CH$_2$), 3.74 (m, 4H, CH$_2$), 4.51 (m, 2H, CH$_2$), 4.61 (m, 2H, CH$_2$), 6.73 (m, 2H, C$_6$*H$_4$*O$_2$), 7.06 (s, 3H, C$_6$*H$_3$*Me$_3$), 7.30 (m, 2H, C$_6$*H$_4$*O$_2$). Anal. Calc. for C$_{25}$H$_{32}$F$_6$O$_{11}$RuS$_2$: C, 38.12; H, 4.09. Found: C, 38.41; H, 4.22%.

4.3. [(mes)Ru(η^6-dibenzo-18-crown-6)](CF$_3$SO$_3$)$_2$ (**2**(OTf)$_2$)

Complex **2**(OTf)$_2$ was obtained analogously to **1**(OTf)$_2$ from [(mes)RuCl$_2$]$_2$ (22 mg, 0.04 mmol), CF$_3$SO$_3$Ag (38 mg, 0.16 mmol), and dibenzo-18-crown-6 (30 mg, 0.08 mmol) as a white solid. Yield: 35 mg, 54%. ^{1}H NMR: δ 2.42 (s, 9H, C$_6$H$_3$*Me$_3$*), 3.85–4.10 (m, 8H, CH$_2$), 4.18 (m, 4H, CH$_2$), 4.45–4.60 (m, 4H, CH$_2$), 6.50 (m, 2H, C$_6$*H$_4$*O$_2$), 6.72 (s, 3H, C$_6$*H$_3$*Me$_3$), 6.85–6.91 (m, 2H, C$_6$*H$_4$*O$_2$), 6.91–6.99 (m, 4H, C$_6$*H$_4$*O$_2$). Anal. Calc. for C$_{31}$H$_{36}$F$_6$O$_{12}$RuS$_2$: C, 42.32; H, 4.12. Found: C, 41.95; H, 4.17%.

4.4. [(μ-η^6:η^6-dibenzo-18-crown-6)Ru$_2$(mes)$_2$](CF$_3$SO$_3$)$_4$ (**3**(OTf)$_4$)

Complex **3**(OTf)$_4$ was obtained analogously to **1** from [(mes)-RuCl$_2$]$_2$ (64 mg, 0.11 mmol), CF$_3$SO$_3$Ag (116 mg, 0.45 mmol), and dibenzo-18-crown-6 (36 mg, 0.1 mmol) as a white solid. The Al$_2$O$_3$ column cannot be used for purification in this case. The product was purified by precipitation with Et$_2$O from CH$_3$NO$_2$ solution. Yield: 134 mg, 96% as a 2:3 mixture of cis- and trans-isomers.

cis-**3**(OTf)$_4$: ^{1}H NMR: 2.48 (s, 18H, C$_6$H$_3$*Me$_3$*), 3.95–4.10 (m, 8H, CH$_2$), 4.47–4.53 (m, 4H, CH$_2$), 4.58–4.64 (m, 4H, CH$_2$), 6.54 (m, 4H, C$_6$*H$_4$*O$_2$), 6.82 (s, 6H, C$_6$*H$_3$*Me$_3$), 7.01 (m, 4H, C$_6$*H$_4$*O$_2$).

trans-**3**(OTf)$_4$: ^{1}H NMR: 2.43 (s, 18H, C$_6$H$_3$*Me$_3$*), 4.04–4.07 (m, 8H, CH$_2$), 4.46–4.53 (m, 4H, CH$_2$), 4.58–4.65 (m, 4H, CH$_2$), 6.56 (m, 4H, C$_6$*H$_4$*O$_2$), 6.76 (s, 6H, C$_6$*H$_3$*Me$_3$) 6.99 (m, 4H, C$_6$*H$_4$*O$_2$).

Anal. Calc. for C$_{42}$H$_{48}$F$_{12}$O$_{18}$Ru$_2$S$_4$: C, 36.05; H, 3.46. Found: C, 35.87; H, 3.69%.

4.5. NMR titration

To the solution of the crown ether complex of certain concentration (ca. 0.02 M) in CD$_3$NO$_2$ sodium salt Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] was added in small portions and ^{1}H NMR spectrum was recorded after each addition. The exact Na$^+$ concentration was determined by the integration of the [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$ signals. One initial (no sodium), 8 intermediate, and one "saturated" (10-fold excess of sodium) spectra were recorded for each sample. The signal of CHCl$_3$ (7.352 ppm) was used as constant. The changes of the aromatic signals of the crown ethers were plotted against the Na$^+$ concentration and the resulting experimental dots were fitted with the calculated K_a curve. The concentrations of equilibrium participants were calculated from the equation: $\delta_{observed} = (C_{free\ crown} \cdot \delta_{free\ crown} + C_{sodium\ crown\ complex} \cdot \delta_{sodium\ crown\ complex})/2$, where $\delta_{free\ crown}$ was taken from the first experiment (no sodium) and $\delta_{sodium\ crown\ complex}$ from the last one (10-fold excess of sodium) [13].

4.6. Electrochemistry

Anhydrous 99.7% propylene carbonate was an Aldrich product. Fluka [NBu$_4$]PF$_6$ (electrochemical grade) was used as supporting electrolyte (0.2 mol dm^{-3}). Cyclic voltammetry was performed in a three-electrode cell containing the glassy carbon working

Table 1
Crystal data and structure refinement parameters for **2**(OTf)$_2$ and *trans*-**3**(OTf)$_4$.

	2(OTf)$_2$	*trans*-**3**(OTf)$_4$
Formula	C$_{31}$H$_{36}$F$_6$O$_{12}$RuS$_2$	C$_{42}$H$_{48}$F$_{12}$O$_{18}$Ru$_2$S$_4$
M	879.79	1399.18
T, K	120	293
Crystal shape	Prism	Prism
Crystal dimensions	$0.30 \times 0.20 \times 0.20$	$0.42 \times 0.34 \times 0.23$
Crystal color	Colorless	Colorless
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Z	4	2
a, Å	17.594(2)	13.9827(17)
b, Å	15.4205(15)	14.0369(17)
c, Å	12.7085(14)	16.1654(19)
α, °	90.00	114.826(2)
β, °	95.013(5)	99.860(3)
γ, °	90.00	101.271(2)
V, Å^3	3434.6(6)	2707.3(6)
d_{calc}, g cm^{-3}	1.701	1.716
μ, cm^{-1}	6.73	8.22
F(0 0 0)	1792	1408
2θmax, °	58	54
Reflections measured	18,198	23,901
Independent reflections (R_{int})	9039 (0.0485)	11,789 (0.0251)
Observed reflections [$I > 2\sigma(I)$]	5290	9032
Number of parameters	466	701
Final $R(F_{hkl})$: R_1	0.0555	0.0520
wR_2	0.1310	0.1387
GOF	1.066	1.056
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.562, −1.098	1.235, −1.744

electrode surrounded by a platinum-spiral counter electrode and the reference electrode mounted with a Luggin capillary. The reference electrode was an aqueous saturated calomel electrode (SCE). A BAS 100 W electrochemical analyzer was used as polarizing unit. Controlled potential coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E^{\circ\prime}$ = +0.33 V *vs.* SCE.

4.7. X-ray diffraction analysis

Crystals of **2**(OTf)$_2$ and *trans*-**3**(OTf)$_4$ were grown by slow diffusion of Et$_2$O into solution of the complexes in nitromethane. Diffraction data were taken using Bruker SMART 1000 CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans]. The substantial redundancy in data allows empirical absorption correction to be applied using multiple measurements of equivalent reflections with sadabs Bruker program [14]. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The posi-

tions of the hydrogen atoms were calculated from the geometrical point of view. The analysis of Fourier density synthesis has revealed that CF$_3$SO$_3$ anions in both structures are strongly disordered. The disorder of these groups was treated using SAME and DFIX instructions. Notable residual densities remain in both structures because of this disorder as well as due to the presence of heavy ruthenium atoms. All calculations were performed using the shelxtl software [15]. Crystal data and structure refinement parameters for **2**(OTf)$_2$ and **3**(OTf)$_4$ are given in Table 1.

Appendix A. Supplementary data

^{1}H NMR spectra of partially separated *cis*- and *trans*-isomers of **3**(OTf)$_4$. Cyclic voltammetric response of **2** in the presence of equimolar amount of ferrocene reference derivative. CCDC 725126 and 725127 contain the supplementary crystallographic data for **2**(OTf)$_2$ and *trans*-**3**(OTf)$_4$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.032.

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