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Synthesis and some properties of binuclear ruthenocene derivatives bridged by both ethene and thiophene derivatives

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Abstract

Binuclear ruthenocenes bridged by ethenes and thiophene derivatives, Rc–CH=CH–Z–Rc and Rc*–CH=CH–Z–CH=CH–Rc* (Z = thiophene, thieno[3,2-*b*]thiophene, and 2,2′-bithiophene; Rc = ruthenocenyl, R* = 1′,2′,3′,4′,5′-pentamethylruthenocenyl) were prepared. These complexes showed a one-step two-electron redox wave in the cyclic voltammograms, in contrast to the benzenoid-bridged dinuclear ruthenocenes. The chemical oxidation of the Rc–CH=CH–Z–Rc complexes gave no stable oxidized species. The two-electron oxidized species of the Rc*–CH=CH–Z–CH=CH–Rc* complexes were comparably stable and contained a fulvene-complex type structure.

Keywords: Ruthenocenes; Thiophene derivatives; Two-electron redox

1. Introduction

Ferrocene derivatives bridged by an unsaturated organic compound have been known as an important subject of the investigation for the electron-transfer and the development of functionalized materials since early times [1]. Especially, the one-electron oxidation of binuclear ferrocene derivatives bridged by ethenes [2], ethynes [3], or thiophene derivatives [4] was one of the main subjects investigating mixed-valence complexes [5]. However, only a few have been studied for ruthenocene derivatives because ruthenocene itself suffers irreversible two-electron oxidation [6]. It has been found that the binuclear ruthenocne derivatives bridged by ethenes [7] or ethynes [8] are subject to reversible one-step two-electron redox process and the spin–coupling of the singlet di-radical cations in the two-electron oxidized species leads to facile structural isomerization. Among aromatic linkers, benzene or naphthalene derivatives were ineffective for the spin–coupling interaction between the two ruthenocenyl sites in the two-electron oxidized species of binuclear ruthenocenes [9], but thiophene derivatives were much effective candidates [10]. Recently, a good reversibility of the ruthenocene oxidation in the analogous complex was reported [11]. These findings stimulate us to study which of an ethene or an aromatic linker can contribute strongly to the spin–coupling in the binuclear ruthenocenes containing both an ethene and thiophene derivatives in the bridge. We here report the synthesis and redox behavior of such systems.

2. Results and discussion

2.1. Synthesis and characterization

2.1.1. Bridging by one ethene and thiophene derivatives

The complexes bridged by one ethene and thiophene derivatives were prepared by way of the route shown in Fig. 1. 4,4,5,5-Tetramethyl-2-ruthenocenyl-1,3-dioxabororane (**1**) was heated with 2-iodothiophene in the presence of catalytic amount of $PdCl_2$(dppf) in 3 M NaOH and

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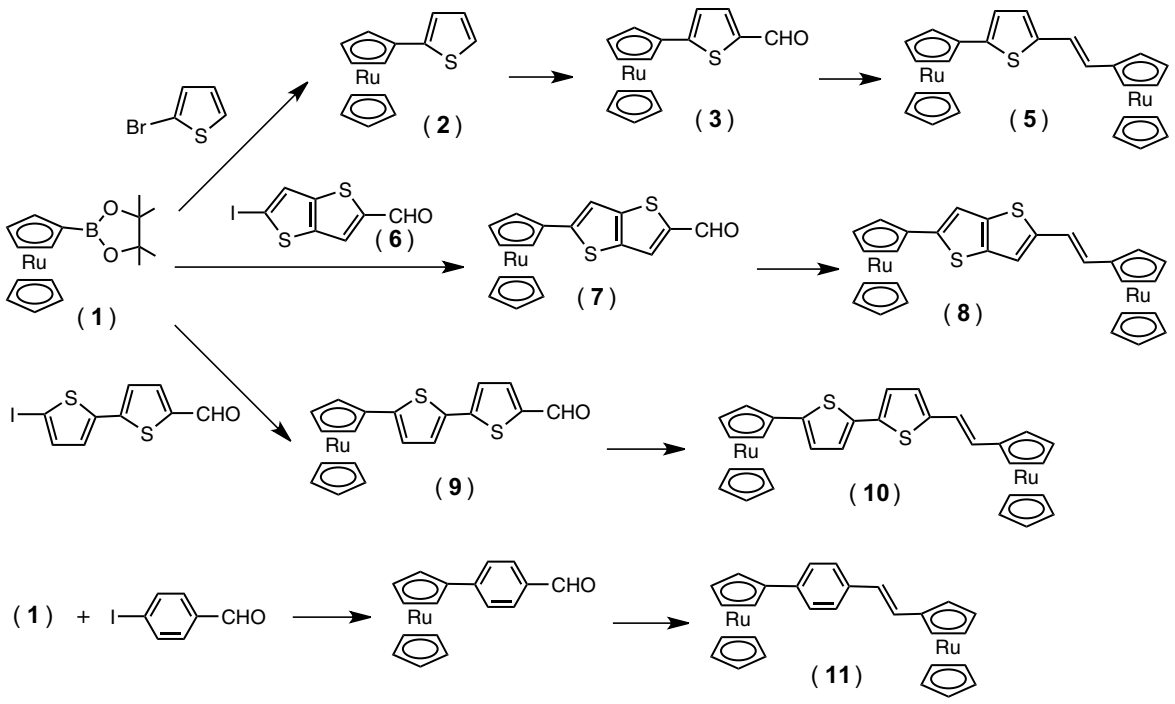
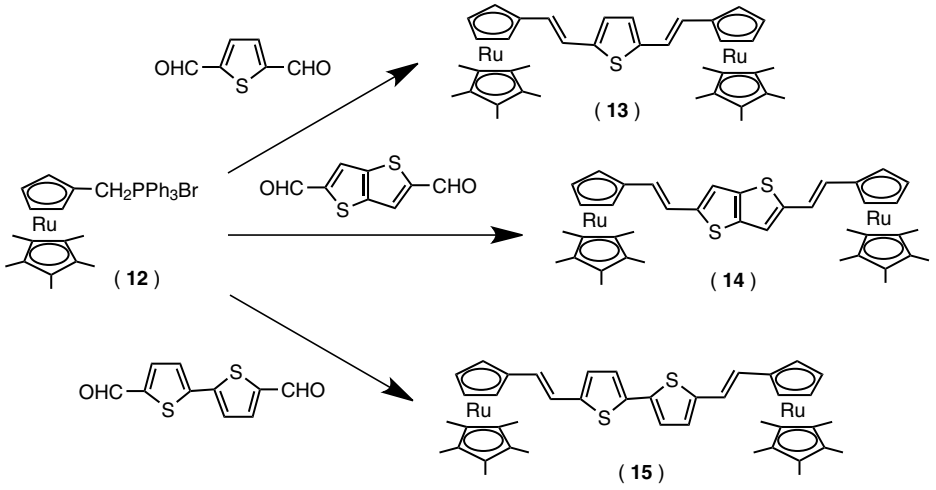


Scheme 1.



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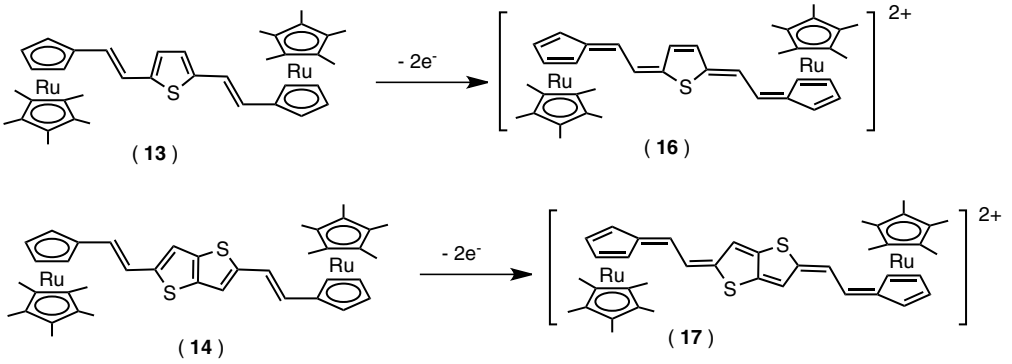

Scheme 3.

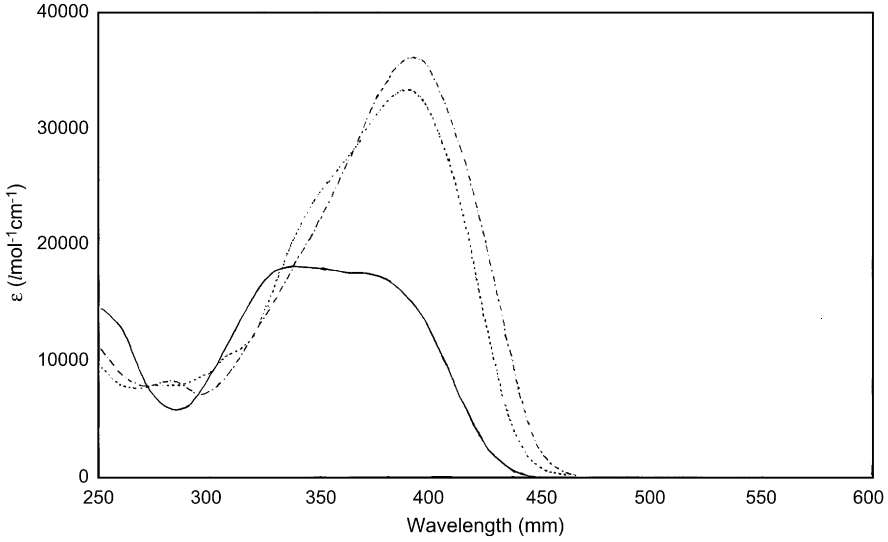

Fig. 1. UV–Vis spectra of complexes **5** (———), **8** (. . .. . .), and **10** (–·–·–·) in CH_2Cl_2.

dimethoxyethane (DME) at 60 °C for 8 h to give 2-ruthenocenylthiophene (**2**) in 60% yield [dppf = 1,1′-bis(diphenylphoshino)ferrocene]. Refluxing of **2** with $POCl_3$ and dimethylformamide (DMF) in dichloroethane for 14 h led to 2-formyl-5-ruthenocenylthiophene (**3**) in 84% yield. The Wittig reaction of **3** with (ruthenocenylmethyl)triphenylphosphonium bromide (**4**) and LDA afforded a mixture of 5-(2′-ruthenocenyl-*E*-ethenyl)-2-ruthenocenylthiophene (**5**) and its *Z* isomer (*E*:*Z* = 30:1) in 64% yield. 2-Formylthieno[3,2-*b*]thiophene reacted with I_2 and HgO in benzene to give 5-iodo-2-formylthieno[3,2-*b*]thiophene (**6**) in good yield. The Pd(II) catalyzed reaction of **6** with the dioxaborolane **1** in alkali and DME led to 5-ruthenocenyl-2-formylthieno[3,2-*b*]thiophene (**7**) in 61% yield. The Wittig reaction of **7** with **4** in the presence of LDA gave 5-(2′-ruthenocenyl-*E*-ethenyl)-2-ruthenocenylthieno[3,2-*b*]thiophene (**8**) in 47% yield. Similarly, the reaction of 5′-formyl-5-iodo-2,2′-bithiophene with the dioxaborolane **1** gave 5′-formyl-5-ruthenocenyl-2,2′-bithiophene (**9**), the Wittig reaction of which led to 5′-(2″-ruthenocenyl-*E*-ethenyl)-5-ruthenocenyl-2,2′-bithiophene (**10**) in 62% yield, along with a trace amount of its *Z*-isomer. The Wittig reaction of 4-ruthenocenylbenzaldehyde, which was prepared from the Suzuki reaction between 4-bromobenzaldehyde and the dioxaborolane **1**, with the phosphonium salt **4** and LDA led to 4-(2′-ruthenocenyl-*E*-ethenyl)-1-ruthenocenylbenzene (**11**) in moderate yield.

2.1.2. Bridging by two ethenes and thiophene derivatives

The Wittig reaction of (1′,2′,3′,4′,5′-pentamethylruthenocenylmethyl)triphenylphosphonium bromide (**12**) and 2,5-diformylthiophene gave 2,5-bis(1′-ethenyl-1″,2″,3″,4″,5″-pentamethylruthenocenyl)thiophene (**13**) in moderate yield, as shown in Fig. 2. In a similar manner, the

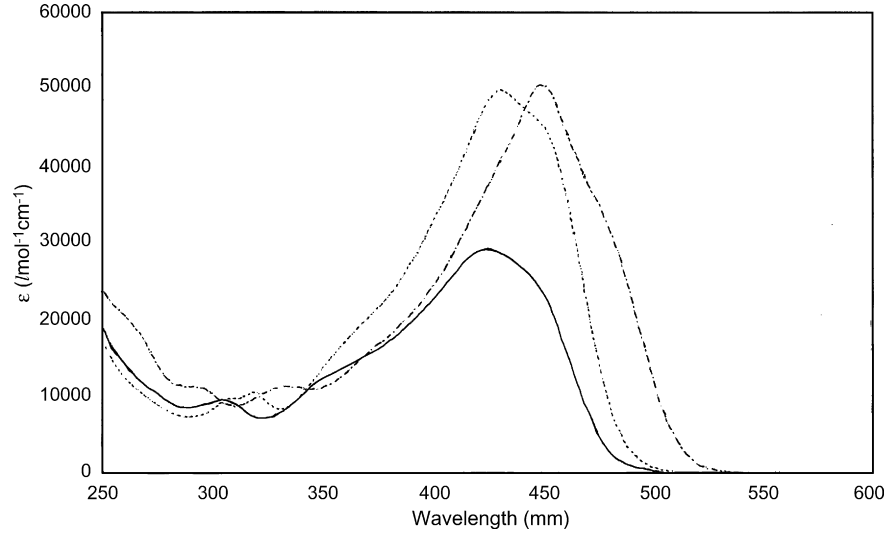

Fig. 2. UV–Vis spectra of complexes **13** (———), **14** (. . . . .), and **15** (–·–·–·) in CH_2Cl_2.

corresponding thieno[3,2-*b*]thiophene (**14**) and 2,2′-bithiophene analogs (**15**) were obtained. The structures of the complexes prepared above were assigned by their IR, ^{1}H and ^{13}C NMR spectra (see Fig. 3).

2.1.3. Electronic spectra

The UV–Vis spectra of the complexes were measured for dichloromethane solutions and their data were summarized in Table 1. The UV–Vis spectra of **5**, **8**, and **10** are shown in Fig. 1 and those of **13**–**15** in Fig. 2. In common, the weak absorption attributed to the d–d transition of ruthenocene (358 nm, ε 200) [12] and pentamethylruthenocene (309 nm, ε 260) is likely buried under the strong absorptions described below. The complexes **5**, **8**, and **10** display two absorption bands with large molecular extinction coefficient. The two absorption in **5** show a red shift by about 30 nm compared with those of 2,5-bis(ruthenocenyl)thiophene [λ 308 (ε 12300) and 355sh (6440)]. The lower energy band at 380 nm in **5** is assigned to the π–π* transition of heteroaromatic segments [13] rather than the d–d transition with the oscillator modified by π-electron system [14], because the π–π* transition band in 1,4-bis(β-ferrocenylvinyl)thiophene was observed at 396 nm and the d–d transition perturbed by π-electron system showed only a little red shift [15]. This assignment is further supported by the fact that extension of conjugation leads to bathochromic shift of π–π* transition and sharp increase in the molecular extinction coefficient (Fig. 1 and Table 1). The higher energy band at 340 nm of **5** may be attributed to charge transfer between the metal and ligand. The complexes **13**–**15** display two absorption bands with large molecular extinction coefficient in lower energy region and two absorption bands with medium intensity in higher energy region. The former two absorptions in **13** shifted to longer wavelength region by 80–100 nm compared with those of 2,5-bis(pentamethylruthenocenyl)thiophene [λ 329 (ε 14200) and 365 (14,700)], which seem to be due to π–π* transition of heteroaromatic segments and/or charge transfer between the metal and ligand. The increase in the intensity and large red shift of these absorption may be due to an increment from charge transfer in the direction of ruthenocene → heteroaromatic segment facilitated by the reduced aromaticity of thiophene derivatives. Two of higher energetic bands remained in a similar region notwithstanding the extension of conjugation or either of them may stem from the d–d transition perturbed by π-electron system.

Table 1
UV–Vis spectral data in CH_2Cl_2

Complex	λ_{max} nm (ε)
5	380 (17000), 339.5 (18300)
8	389 (33500), 358sh (27000)
10	392.5 (36200), 282 (8300)
13	444sh (25600), 425 (29100), 358sh (13900), 304 (9900)
14	449sh (45800), 432 (50200), 370sh (20600), 318 (10800)
15	474sh (35900), 451 (50600), 362sh (13800), 334 (11600)

2.2. Cyclic voltammetry

The cyclic voltammograms of **5**, **8**, **10**, **11** and **13**–**15** were measured in a solution of 0.1 M *n*-Bu_4NClO_4 in CH_2Cl_2 at a glassy carbon electrode and a sweep rate of 0.1 V s^{-1}. The electrochemical data for their first oxidation waves are summarized in Table 2 and the cyclic voltammograms of **5**, **8**, **10**, and **11** are exhibited in Fig. 3, and those of **13**–**15** in Fig. 4. As seen in Figs. 3 and 4, the cyclic vol-

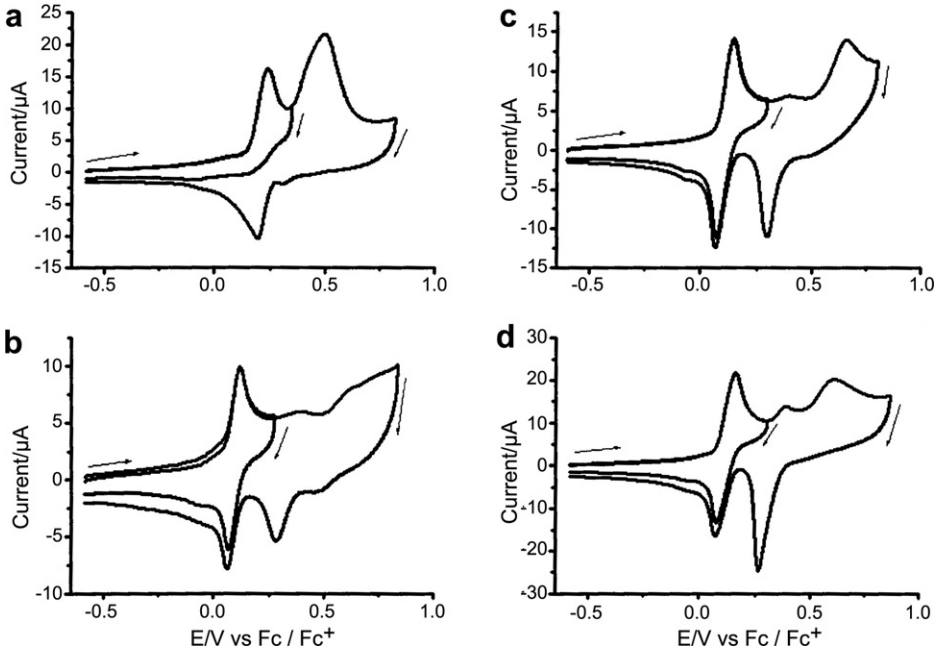

Fig. 3. Cyclic voltammograms of complexes **11** (a), **5** (b), **8** (c), and **10** (d) measured in 1 M (*n*-Bu)$_4$$NClO_4$ solution in CH_2Cl_2.

Table 2
The electrochemical data for the first oxidation wave of complexes[a]

Complex	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE (mV)	I_{pa} (U)[b]	i_{pc}/i_{pa}	n[c]
5	0.12	0.07	0.09	50	2200	1.0	[d]
8	0.15	0.07	0.11	77	2320	1.0	[d]
10	0.16	0.08	0.12	85	1680	0.9	1.85(12)
11	0.24	irr.	0.24[e]	irr.	1140	irr.	1.18(4)
13	−0.14	−0.24	−0.19	100	2000	1.0	1.80(9)
14	−0.08	−0.17	−0.13	92	1860	1.0	2.01(10)
15	−0.03	−0.13	−0.08	95	2000	1.0	1.95(9)

[a] Sweep rate = 0.1 V s^{-1}.
[b] I_{pa} current parameter = $i_{pa}/(A.C.V^{1/2})$; $U = \mu$ A cm^{-2} mM^{-1} $V^{-1/2}$ $s^{1/2}$.
[c] Determined by thin-layer coulometry.
[d] The reliable measurement could not be carried out because of the insolubility.
[e] The value at sweep rate of 1 V s^{-1}.

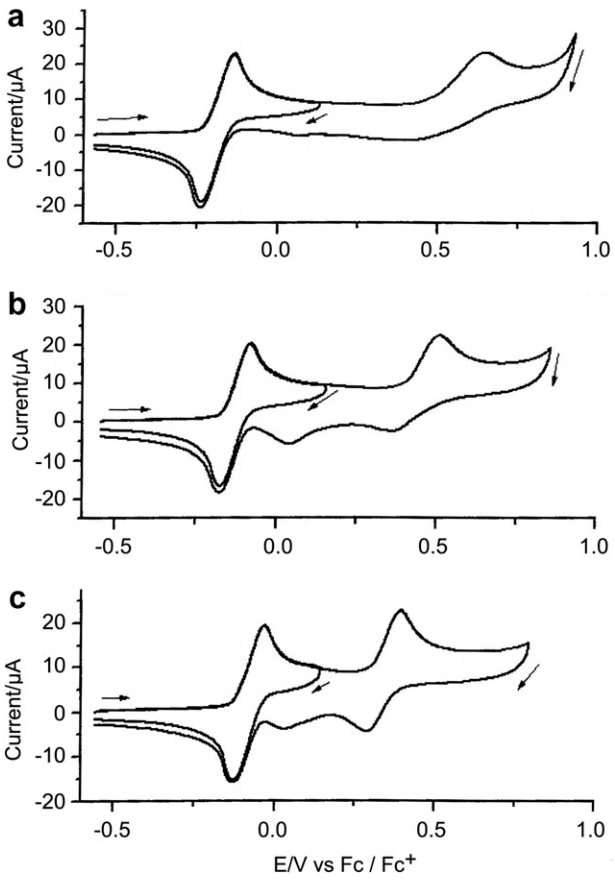

Fig. 4. Cyclic voltammograms of complexes **13** (a), **14** (b), and **15** (c) measured in 1 M $(n\text{-Bu})_4NClO_4$ solution in CH_2Cl_2.

tammograms were much more complex than those of bis(ruthenocenyl)ethenes reported previously, in which only a pair of oxidation and reduction wave was observed in a similar region [7]. However, the cyclic voltammograms exhibited a definite oxidation wave near 0.15 V in **5**, **8**, and **10**, and near 0.0 V in **13**–**15**, which was accompanied with the reductive wave with a nearly equal intensity. If the scan turned back at 0.25 V when the positive scan finished up to record the first wave, the ratio i_{pa}/i_{pc} was nearly 1.0, as seen in Table 1. This performance is similar to that in bis(ruthenocenyl)ethenes, but differs greatly from the finding that the dinuclear ruthenocene derivatives bridged by benzenoid aromatics only show a small or no oxidation wave near 0.3 V [9]. As shown in Table 1, the n value in the thin-layer coulometry was approximately 2 and the peak current parameter I_{pa} was about 2000, suggesting that the first oxidation wave near 0.15 V in **5**, **8**, and **10** and near 0.0 V in **13**–**15** can be assigned to the one-step two-electron process that corresponds to the Ru(II)/Ru(III) couple at the two ruthenocenyl sites. Along with these waves, their cyclic voltammograms all are attended by the irreversible oxidation wave near 0.5 V. Such behavior also resembles with those of dinuclear ruthenocene derivatives bridged by only thiophene derivatives [10]. The magnitude of the wave near 0.5 V was nearly equal to that of the wave near 0.15 V in **5**, **8**, and **10** and near 0.0 V in **13**–**15**. These observations suggest that the second oxidation wave of these complexes may be assigned to the two-electron oxidation process corresponding to the Ru(III)/Ru(IV) couple in the two ruthenocenyl sites, because mononuclear ruthenocene shows irreversible oxidation wave of a Ru(II)/Ru(IV) couple at 0.55 V. The observation of the first oxidation wave at low-potential region suggests that the two-electron oxidized species of complexes **5**, **8**, and **10**, and **13**–**15** may be stable.

It is noteworthy that the oxidation wave for **5** (+ 0.12 V) is observed in a lower potential region than that of 2, 5-bis(ruthenocenyl)thiophene (0.24 V) [10]. This may be due to the incorporation of the ethene part in the bridge of **5**, because the oxidation wave in bis(ruthenocenyl)ethene appeared at +0.03 V [7]. It is also interesting that the cyclic voltammogram of 4-(ruthenocenylethenyl)-1-ruthenocenylbenzene (**11**) shows the oxidation wave at 0.25 V, although 1,4-bis(ruthenocenyl)benzene exhibits only the irreversible four-electron oxidation wave near 0.5 V [9]. The electrochemical behavior of **11** is fairly different from that of other complexes as indicated in Fig. 3 and Table 1. The first oxidation process was irreversible and the n value is near 1. This seems to be probably because the insertion of a benzene ring to the bridge disturbs the spin–coupling interaction between the two ruthenocenyl sites. Nevertheless, the appearance of the first oxidation wave at low-potential region suggests that the ruthenocenylethenyl moiety also play an important part in the oxidation of this complex. The oxidation potential for **5** (0.12 V) is lower than that of **11** (0.25 V), being probably because the smaller aromaticity and the more electron-richness in the thiophene ring compared with those in a benzene ring promotes the one-step two-electron redox process. The substitution of the ruthenocene ring by the methyl group also seems to assist the one-step two-electron redox process, although the effect of the increased ethene bond cannot be disregarded. For example, in the cyclic voltammograms for **13**–**15** the oxidation potentials are observed near −0.10 V and are significantly lower than that of the Rc series. It is worthy to notice that the oxidation potentials in the present complexes influence little or a little with

the increase of conjugation in the linker: **5** (+0.12 V), **8** (+0.15 V), **4** (+0.16 V); **13** (−0.14 V) < **14** (−0.08 V) < **15** (−0.03 V). A similar trend is also observed in the binuclear ruthenocene bridged by thiophene derivatives [10]. However, this tendency is different from that observed in the $Rc^*(CC)_nRc^*$ series [8], in which the oxidation potentials shift to higher potential region with the increase of conjugation in the linker. By contrast, in the dinuclear ruthenocene derivatives bridged by oligoenes, the oxidation potentials shift to lower potential region with the increase of the number of CH=CH units [7]. This little influence of conjugation in the present series seems to be probably related to the fact that the aromaticity in the thiophene ring works in greater or less as cross-conjugation with the electronic interaction between two metal sites in the two-electron oxidized species of the present complexes.

2.3. Chemical two-electron oxidation

The oxidation of **5**, **8**, and **10** with two equivalent of p-benzoquinone (hereafter abbreviated as *p*-BQ) and BF_3OEt_2 in CH_2Cl_2 generated red-violet solution and gave black crystalline products in the dilution with diethyl ether. However, the solution of them in CD_3NO_2 gave only a complex ^1H NMR spectrum, suggesting that the two-electron oxidized species of the unsymmetrical system (**5**, **8**, and **10**) is unstable in solution. Similar oxidation of **13** and **14** afforded dark-purple and dark-blue crystalline solids **16a** and **17a**, respectively. The oxidation of **13** with 2 equivalents of $FcH^+BAr_4^-$ [Ar = 3,5-bis(trifluoromethyl)phenyl] also afforded a stable dark-purple needles (**16b**) in a quantitative yield. Complex **14** was not oxidized with $FcH^+BAr_4^-$, but could be oxidized with *p*-BQ/$NaBAr_4$ in CH_2Cl_2 to give a stable purple needles (**17b**) in good yield. The solution of **16a** and **16b** in CD_3NO_2 were relatively stable, the ^1H NMR spectra of which are similar and showed that the solution was a mixture of some compounds. The main signals for the η-C_5H_4 ring protons appeared at δ 5.02, 5.44, 5.79, and 5.85 as multiplets. The pattern of appearance for them is similar to that in the two-electron oxidized species of bis(pentamethylruthenocenyl)ethene (δ 4.93, 5.43, 5.60, and 5.86) [7b], suggesting that the major components of **16** in the solution contain the complex with a fulvene complex-type structure. On addition to these signals, there were two singlets near δ 6.4 and a pair of doublets ($J = 12.6$ Hz) near δ 6.3 and 6.9. Complex **16**, therefore, has a high possibility to be a mixture of conformers containing the fulvene complex-type structure. This is different from the oxidized species in bis(ruthenocenyl)ethenes in which no conformer was observed [7].

The deep blue solution of **17a** and **17b** in CD_3NO_2 was unstable. The ^1H NMR spectra of the cationic part of **17a** and **17b** right after preparation is similar and showed that the solution consisted of almost single component. In the spectrum, the methyl proton of the Cp^* ring was observed at δ 1.95 as a singlet, the η-C_5H_4 ring protons at δ 5.00, 5.44, 5.73, 5.81 as a broad singlet, the protons of the original ethene part at δ 6.49 and 6.65 as doublets ($J = 13$ Hz), and the thieno[3,2-*b*]thiophene ring protons at δ 7.13 as a singlet. This suggests that the oxidized species **17a** and **17b** also have a fulvene-complex type structure.

3. Experimental

All reactions were carried out under an atmosphere of N_2 and/or Ar and workups were performed without precaution to exclude air. NMR spectra were recorded on Bruker AC300P, AM400 or ARX400 spectrometer. IR (KBr disc) spectra were recorded on Perkin–Elmer System 2000 spectrometer. Cyclic voltammetric and thin-layer coulometric measurements [16] were carried out with an ALS 400A Electrochemical Analyzer at 20 °C. A three-electrode cell containing of a glassy carbon disk working electrode (diameter 0.3 cm), Pt-coil counter electrode and Ag/AgCl (3M NaCl) reference electrode were employed. The ferrocene/ferricenium(Fc/Fc^+) redox couple was used as an internal standard of the potential. Tetrabutylammonium tetrafluoroborate $(n\text{-}Bu)_4BF_4$ (Nacalai Tesque Inc.) was purified by recrystallization to be used as a supporting electrode. Prior to the electrochemical measurements, all solutions were degassed with high-purity Ar. Dry solvents were prepared by distillation from the drying agent prior to use as follows: CH_2Cl_2 ($CaCl_2$); $ClCH_2CH_2Cl$ ($CaCl_2$); benzene (Na); THF (Na-benzophenone); DMF (CaH_2). 2-Ruthenocenyl-1,3-dioxaborolane (**1**) [9], ruthenoceny(triphenyl)phosphonium bromide (**4**) [7c], 1′,2′,3′,4′,5′-pentamemylruthenocenyl(triphenyl)phosphonium bromide (**12**) [7c], 2-formylthieno[3,2-*b*]thiophene [17], 2,5-diformylthieno[3,2-*b*]thiophene [18], 5′ formyl-5-iodo-2,2′-bithiophene [19], 5,5′-diformyl-2,2′-bithiophene [19], dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium, (dppf)$PdCl_2$ [20], $Na^+[BAr_4']^-$ [21] and $FcH^+[BAr_4']^-$ [22] were prepared according to the literatures. Other reagents were used as received from commercial suppliers.

3.1. 2-Ruthenocenylthiophene (2)

A mixture of 4,4,5,5-tetramethyl-2-ruthenocenyl-1,3-dioxabororane (**1**) (0.36 g, 1 mmol), 2-iodothiophene (0.2 ml, 2 mmol), $PdCl_2$(dppf) (40 mg) in 3 M aqueous NaOH solution and DME (15 ml) was heated at 60 °C for 8 h under Ar. After cooling, the mixture was diluted with CH_2Cl_2. The mixture was washed twice with H_2O and dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 with elution of hexane/benzene to give the title complex (190 mg, 60%) and ruthenocene (17 mg, 7%). Pale yellow crystals. M.p. 94 °C. Anal. Calc. for $C_{14}H_{12}SRu$: C, 53.65; H, 3.86. Found: C, 53.65; H, 3.73%. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.51 (s, 5H, η-C_5H_5), 4.61 (dd, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.98 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 6.86 (dd, $J = 5.2$ and 3.7 Hz, 1H, 4-H), 6.94 (dd, $J = 5.2$ and 1.1 Hz, 1H, 3-H), and 7.09 (dd, $J = 5.2$ and 1.1 Hz, 1 H, 5-H). ^{13}C NMR ($CDCl_3$,

100 MHz): δ 70.26 (η-C_5H_4), 70.46 (η-C_5H_4), 71.76 (η-C_5H_5), 84.00 (η-C_5H_4-*ipso*), 123.12 (C-3 or C-4), 123.32 (C-3 or C-4), 126.90 (C-2), 142.30 (C-2).

3.2. 2-Formyl-5-ruthenocenylthiophene (**3**)

A solution of $POCl_3$ (0.2 ml, 2.7 mmol) and DMF (0.2 ml, 2.2 mmol) in dichloroethane (8 ml) was stirred for 30 min at room temperature under Ar. To the solution was slowly added a solution of **2** (0.16 g, 0.5 mmol) in dichloroethane (2 ml) and the solution was refluxed for 14 h. After cooling, the solution was poured into saturated aq. Na_2CO_3 solution. The mixture was extracted with CH_2Cl_2. The extract was washed with saturated aq. LiCl solution and water, and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 with elution of CH_2Cl_2 to give the title complex (144 mg, 84%). M.p. 123 °C. Anal. Calc. for $C_{17}H_{14}OSRu$: C, 60.89; H, 4.21. Found: C, 60.62; H, 4.03%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.52 (s, 5H, η-C_5H_5), 4.71 (t, $J = 1.8$ Hz, 2 H, η-C_5H_4), 5.07 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 7.03 (d, $J = 3.9$ Hz, 1H, 4-H), 7.53 (d, $J = 3.9$ Hz, 1H, 3-H), and 9.80 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.19 (η-C_5H_4), 71.66 (η-C_5H_5), 72.30 (η-C_5H_4), 81.67 (η-C_5H_4-*ipso*), 123.64 (C-4), 137.23 (C-3), 140.60 (C-5), 154.76 (C-2), and 182.54 (CHO).

3.3. 5-(2′-Ruthenocenyl-E-ethenyl)-2-ruthenocenylthiophene (**5**)

To a suspension of the phosphonium salt **4** (0.32 g, 0.55 mmol) in THF (10 ml) was added lithium diisopropylamide (LDA) (2 mmol) in THF (5 ml) blow −78 °C under Ar. The mixture was stirred for 30 min and then a solution of **3** (0.17 g, 0.48 mmol) in THF (5 ml) was added to the mixture. After being warmed gradually to room temperature, the mixture was stirred for 1 h and then refluxed for 3 h. After hydrolysis with saturated aq. NH_4Cl solution, the mixture was extracted with CH_2Cl_2. The extract was washed with H_2O twice and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 with elution of hexane/benzene to give the title complex (*E*:*Z* = 30:1 from ^{1}H NMR spectrum) in 64% yield. Fractional recrystallization from EtOH gave pure *E*-isomer. M.p. 212 °C. Anal. Calc. for $C_{26}H_{22}SRu_2$: C, 54.92; H, 3.90. Found: C, 55.32; H, 4.09%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.52 (s, 5H, η-C_5H_5), 4.54 (s, 5H, η-C_5H_5), 4.60 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.62 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.82 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.96 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 6.43 (d, $J = 15.9$ Hz, =CH), 6.64 (d, $J = 3.9$ Hz, 1H, 3- or 4-H), 6.67 (d, $J = 15.9$ Hz, =CH), and 7.53 (d, $J = 3.9$ Hz, 1H, 3- or 4-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 68.94 (η-C_5H_4), 69.80 (η-C_5H_4), 70.54 (η-C_5H_4), 70.67 (η-C_5H_5), 71.14 (η-C_5H_4), 71.82 (η-C_5H_5), 84.00 (η-C_5H_4-*ipso*), 87.32 (η-C_5H_4-*ipso*), 119.56 (C-3 or C-4), 123.39 (C-3 or C-4), 124.84 (=CH), 128.32 (=CH), 140.41 (C-2 or C-5), 140.97 (C-2 or C-5).

3.4. 2-Formyl-5–iodothieno[3,2-*b*]thiophene (**6**)

A mixture of 2-formylthieno[3,2-*b*]thiophene (0.27 g, 1.6 mmol), HgO (1.8 g, 8.2 mmol), and I_2 (2.06 g, 7.8 mmol) in benzene (15 ml) was stirred for 8 h at 70 °C. The mixture was filtered and the filtrate was washed saturated aq. NaS_2O_3 solution. The solution was dried over $MgSO_4$ and then evaporated under reduced pressure. The residue was purified by a chromatography on SiO_2. Yield: 0.33 g (70%). M.p. 185–186 °C. Anal. Calc. for $C_7H_3IOS_2$: C, 28.58; H, 1.03. Found: C, 28.29; H, 0.89%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52 (s, 1H, 3-H), 7.85 (s, 1H, 6-H), and 9.99 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 127.52 (C-3 or C-6), 129.16 (C-3 or C-6), 143.72, 144.80, 145.76, 183.56 (CHO).

3.5. 2-Formyl-5-ruthenocenylthieno[3,2-*b*]thiophene (**7**)

A mixture of **6** (20 mg, 0.08 mmol), **1** (30 mg, 0.09 mmol), $Pd(PPh_3)_4$ (12 mg), $CsCO_3$ (40 mg, 0.1 mmol) in 3 M aq. NaOH (2 ml) and DME (8 ml) in sealed tube was heated at 70 °C for 10 h. The reaction mixture was washed out with CH_2Cl_2. The solution was washed with H_2O twice and dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 with elution of CH_2Cl_2 to give the title complex (20 mg). M.p. 213–214 °C. Anal. Calc. for $C_{17}H_{12}OS_2Ru$: C, 51.37; H, 3.04. Found: C, 51.38; H, 2.97%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.54 (s, 5H, η-C_5H_5), 4.71 (t, $J = 2.2$ Hz, 2H, η-C_5H_4), 5.06 (t, $J = 2.2$ Hz, 2H, η-C_5H_4), 7.17 (s, 1H, 6-H), and 7.81 (s, 1H, 3-H), and 9.91 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.09 (η-C_5H_4), 71.43 (η-C_5H_4), 72.22 (η-C_5H_5), 82.74 (η-C_5H_4-*ipso*), 115.20 (C-6), 129.18 (C-3), 137.16, 143.67, 152.81, 183.03 (CHO).

3.6. 5-(2′-Ruthenocenyl-E-ethenyl)-2-ruthenocenylthieno-[3,2-*b*]thiophene (**8**)

This complex was prepared from **7** (0.17 g, 0.42 mmol) and **4** (0.27 g, 0.46 mmol) according to the procedure similar to that described in Section 3.3. The product (0.19 g, 70%) was a 2:1 mixture of *E*- and *Z*-isomers (from ^{1}H NMR spectrum). Fractional recrystallization gave pure *E*-isomer. M.p. >250 °C. Anal. Calc. for $C_{18}H_{22}S_2Ru_2$: C, 53.83; H, 3.55. Found: C, 53.59; H, 3.35%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.52 (s, 5H, η-C_5H_5), 4.54 (s, 5H, η-C_5H_5), 4.62 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.65 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.84 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 5.01 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 6.52 (d, $J = 15.9$ Hz, =CH), 6.76 (d, $J = 15.9$ Hz, =CH), 6.93 (s, 1H, 3- or 6-H), and 7.03 (s, 1H, 3- or 6-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.05 (η-C_5H_4), 69.88 (η-C_5H_4), 70.71 (η-C_5H_4), 70.83 (η-C_5H_4), 71.20 (η-C_5H_5), 71.93 (η-C_5H_5), 110.95 (=CH), 115.30 (=CH), 116.83 (=CH), 125.41 (=CH). No quaternary carbons were observed because of insolubility.

3.7. 5′-Formyl-5-ruthenocenyl-2,2′-bithiophene (**9**)

This complex was prepared from 5′-formyl-5-iodo-2,2′-bithiophene (0.02 g, 0.07 mmol) and **1** (0.03 g, 0.09 mmol) according to the procedure similar to that described in Section 3.5. Yield: 21 mg (76%). M.p. 182 °C. Anal. Calc. for $C_{19}H_{14}OS_2Ru$: C, 53.88; H, 3.33. Found: C, 53.61; H, 3.27%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.53 (s, 5H, η-C_5H_5), 4.67 (t, $J = 2.2$ Hz, 2H, η-C_5H_4), 5.01 (t, $J = 2.2$ Hz, 2H, η-C_5H_4), 6.90 (d, $J = 3.7$ Hz, 1H, 3-H), 7.13 (d, $J = 3.7$ Hz, 1H, 4-H), 7.17 (d, $J = 4.1$ Hz, 1H, 4′-H), 7.65 (d, $J = 7.1$ Hz, 1H, 3′-H), and 9.84 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.00 (η-C_5H_4), 71.01 (η-C_5H_4), 72.05 (η-C_5H_5), 82.64 (η-C_5H_4-*ipso*), 123.39 (Th–CH), 124.09 (Th–CH), 126.39 (Th–CH), 133.14, 137.42 (Th–CH), 141.09, 145.45, 147.64, and 182.36 (CHO). (Th = thiophene).

3.8. 5′-(2″-Ruthenocenyl-E-ethenyl)-5-ruthenocenyl-2, 2′-bithiophene (**10**)

This complex was prepared from **9** (0.17 g, 0.42 mmol) and **4** (0.27 g, 0.46 mmol) according to the procedure similar to that described in Section 3.3. The product (0.17 g, 62%) was a 30:1 mixture of *E*- and *Z*-isomers (from ^{1}H NMR spectrum). Fractional recrystallization gave pure *E*-isomer. M.p. 170 °C. Anal. Calc. for $C_{30}H_{24}S_2Ru_2$; C, 55.37; H, 3.72. Found: C, 55.33; H, 3.68%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.53 (s, 5H, η-C_5H_5), 4.54 (s, 5H, η-C_5H_5), 4.62 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.64 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.83 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 4.98 (t, $J = 1.8$ Hz, 2H, η-C_5H_4), 6.51 (d, $J = 15.8$ Hz, =CH), 6.70 (d, $J = 15.8$ Hz, =CH), 6.77 (d, $J = 3.7$ Hz, 1H, Th–CH), and 6.83 (d, $J = 3.7$ Hz, 1H, Th–CH), 6.90 (d, $J = 3.7$ Hz, 1H, Th–CH), and 6.94 (d, $J = 3.7$ Hz, 1H, Th–CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.04 (η-C_5H_4), 69.92 (η-C_5H_4), 70.65 (η-C_5H_4), 70.81 (η-C_5H_4), 71.18 (η-C_5H_5), 71.89 (η-C_5H_5), 83.50 (η-C_5H_4-*ipso*), 87.00 (η-C_5H_4-*ipso*), 119.06, 123.31, 123.80, 125.45, 125.80, 128.32, 135.10, 135.25, 141.60, and 141.97.

3.9. 4-Ruthenocenylbenzaldehyde

This complex was prepared from 4-bromobenzaldehyde (0.58 g, 3.1 mmol) and **1** (0.36 g, 1.0 mmol) according to the procedure similar to that described in Section 3.5. Yield: 93 mg (29%). M.p. 134–135 °C. Anal. Calc. for $C_{17}H_{14}ORu$: C, 60.89; H, 4.21. Found: C, 60.62; H, 4.03%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.47 (s, 5H, η-C_5H_5), 4.74 (t, $J = 1.4$ Hz, 2H, η-C_5H_4), 5.11 (t, $J = 1.4$ Hz, 2H, η-C_5H_4), 7.52 (d, $J = 8.2$ Hz, 2H, 3,5-H), 7.73 (d, $J = 8.2$ Hz, 1H, 2,6-H), and 9.94 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.59 (η-C_5H_4), 71.77 (η-C_5H_4), 71.80 (η-C_5H_5), 87.59 (η-C_5H_4-*ipso*), 126.39 (Ph–CH), 129.74, 129.83 (Ph–CH), 146.21, and 191.62 (CHO).

3.10. 4-(2′-Ruthenocenyl-E-ethenyl)-1-ruthenocenylbenzene (**11**)

This complex was prepared from 4-ruthenocenylbenzaldehyde (0.17 g, 0.5 mmol) and **4** (0.32 g, 0.55 mmol) according to the procedure similar to that described in Section 3.3. M.p. >250 °C. Anal. Calc. for $C_{18}H_{24}Ru_2 \cdot \frac{1}{2}C_6H_6$: C, 61.88; H, 4.52. Found: C, 61.98; H, 4.36%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.46 (s, 5H, η-C_5H_5), 4.53 (s, 5H, η-C_5H_5), 4.61 (t, $J = 1.5$ Hz, 2H, η-C_5H_4), 4.65 (t, $J = 1.5$ Hz, 2H, η-C_5H_4), 4.86 (t, $J = 1.5$ Hz, 2H, η-C_5H_4), 5.02 (t, $J = 1.5$ Hz, 2H, η-C_5H_4), 6.59 (d, $J = 16.1$ Hz, =CH), 6.72 (d, $J = 16.1$ Hz, =CH), 7.22 (s, 1H, 2, 6-H), and 7.32 (s, 1H, 3, 5-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.10 (η-C_5H_4), 69.29 (η-C_5H_4), 70.67 (η-C_5H_4), 70.80 (η-C_5H_5), 71.09 (η-C_5H_4), 71.45 (η-C_5H_5), 87.65 (η-C_5H_4-*ipso*), 89.88 (η-C_5H_4-*ipso*), 125.02 (Ph–CH), 125.61 (=CH), 126.63 (=CH), 128.32 (Ph–CH), 135.58, 137.05.

3.11. 2,5-Bis{2′-(1″,2″,3″,4″,5″-pentamethylruthenocenyl) ethenyl}thiophene (**13**)

To a suspension of (1″,2″,3″,4″,5″-pentamethylruthenocenylmethyl)triphenylphosphonium bromide (1.0 g, 1.5 mmol) in THF (10 ml) was slowly added LDA (2.4 mmol) below −78 °C and then the mixture was stirred for 30 min. 2,5-Diformylthiophene (0.11 g, 0.75 mmol) was added to the mixture below −78 °C and then the mixture was gradually warmed to room temperature. The mixture was stirred for 2.5 h at the same temperature. The mixture was again chilled below −78 °C and LDA (1.2 mmol) was added to the mixture. The mixture was slowly warmed to room temperature and then hydrolyzed by saturated aqueous NH_4Cl solution (50 ml). The mixture was extracted with CH_2Cl_2. The extract was washed with H_2O and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on Al_2O_3 by elution of hexane/benzene/diethyl ether (10/2/1) to give brown crystals, which was recrystallized from benzene/ethanol. Yield: 0.24 g (43%). M.p. 215°C. Anal. Calc. for $C_{38}H_{44}SRu_2$: C, 62.10; H, 6.03. Found: C, 62.06; H, 5.99%. IR (KBr): 1627 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.87 (30H, Me), 4.28 (t, $J = 1.8$ Hz, 4H, η-C_5H_4), 4.36 (t, $J = 1.8$ Hz, 4H, η-C_5H_4), 6.32 (d, $J = 15.8$ Hz, 2H, =CH), 6.55 (d, $J = 15.8$ Hz, 2H, =CH), and 6.71 (s, 2H, thiophene). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.82 (Me), 71.07 (η-C_5H_4), 73.56 (η-C_5H_4), 85.53 (η-C_5H_4), 85.69 (η-C_5Me_4), 117.85 (Th-2,5), 124.61 (=CH), 125.53 (=CH), 141.20 (Th-3,4).

3.12. 2,5-Bis{2′-(1″,2″,3″,4″,5″-pentamethylruthenocenyl) ethenyl}thieno[3,2-b]thiophene (**14**)

To a mixture of (1″,2″,3″,4″,5″-pentamethylruthenocenylmethyl)triphenylphosphonium bromide (0.67 g, 1.0 mmol) and 2,5-diformylthieno[3,2-*b*]thiophene (98 mg, 0.50 mmol)

in THF (40 ml) was added LDA (3.2 mmol) at 0 °C and then the mixture was warmed to room temperature. After being stirred for 18 h at the same temperature, the mixture was again chilled at 0 °C and LDA (1.2 mmol) was added. The mixture was warmed to room temperature and then stirred for 24 h. The mixture was poured into H_2O (50 ml). The mixture was extracted with benzene and the extract was washed with H_2O and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on Al_2O_3 (deactivated with 5% H_2O) by elution of benzene to give brown crystals, which was recrystallized from benzene/ethanol. Yield: 0.14 g (36%). M.p. >250 °C. Anal. Calc. for $C_{40}H_{44}S_2Ru_2$: C, 90.73; H, 5.54. Found: C, 60.96; H, 5.54%. IR (KBr): 1624 cm^{-1} ($\nu_{C=C}$). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.87 (30H, Me), 4.29 (t, $J = 1.7$ Hz, 4H, η-C_5H_4), 4.37 (t, $J = 1.7$ Hz, 4H, η-C_5H_4), 6.37 (d, $J = 15.8$ Hz, 2H, =CH), 6.63 (d, $J = 15.8$ Hz, 2H, =CH), and 6.95 (s, 2H, Th). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.81 (Me), 71.12 (η-C_5H_4), 73.74 (η-C_5H_4), 85.16 (η-C_5H_4), 85.77 (η-C_5Me_4), 116.20 (Th), 118.02 (=CH), 125.90 (=CH), 136.90 (Th), 145.63 (Th).

3.13. 2,2′-Bis{1″-(1″,2″,3″,4″,5″-pentamethylruthenocenyl) ethenyl}-5,5′-bithiophene (*15*)

This complex was prepared by the procedure described above. Brown crystals (39%). M.p. >237 °C. Anal. Calc. for $C_{40}H_{44}S_2Ru_2$: C, 60.73; H, 5.54. Found: C, 60.96; H, 5.54%. IR (KBr): 1621 cm^{-1} ($\nu_{C=C}$). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.87 (30H, Me), 4.29 (t, $J = 1.7$ Hz, 4H, η-C_5H_4), 4.37 (t, $J = 1.7$ Hz, 4H, η-C_5H_4), 6.35 (d, $J = 15.8$ Hz, 2H, =CH), 6.57 (d, $J = 15.8$ Hz, 2H, =CH), 6.77 (d, $J = 3.7$ Hz, 2H, Th) and 6.98 (d, $J = 3.7$ Hz, 2H, Th). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.82 (Me), 71.18 (η-C_5H_4), 73.75 (η-C_5H_4), 85.27 (η-C_5H_4), 85.82 (η-C_5Me_4), 117.30 (Th), 123.68 (Th), 124.80 (=CH), 126.29 (=CH), 134.49 (Th), 142.96 (Th).

3.14. Two-electron oxidation of *13*

(a) To a solution of **13** (7.4 mg, 0.01 mmol) and *p*-benzoquinone (2.1 mg, 0.02 mmol) in CH_2Cl_2 (3 ml) was added BF_3OEt_2 (1 drop from a capillary) at 0 °C under nitrogen. The resulting deep blue solution was stirred for 15 min, then diluted with dry diethyl ether (10 ml), and kept for 1.5 h at 0 °C. Filtration gave dark blue crystalline solids (6.8 mg, 83%). This product consisted of several species. The ^1H NMR spectrum of the major component (400 MHz, CD_3NO_2): δ 1.97 (s, 30H), 5.04 (m, 2H, η-C_5H_4), 5.46 (m, 2H, η-C_5H_4), 5.81 (m, 2H, η-C_5H_4), 5.87 (m, 2H, η-C_5H_4), 6.31 (m, 2H, =CH), 6.43 (s, 2H, Th-ring), 6.93 (m, 2H, =CH).

(b) To a solution of **13** (7.4 mg, 0.1 mmol) in CH_2Cl_2 (3 ml) was added $FcH^+[BAr'_4]^-$ (21 mg, 0.02 mmol) under stirring at 0 °C under Ar. After stirring for 15 min, dry benzene (3 ml) was added and the solution was kept for 4 h at 0 °C, which resulted in dark-violet crystals. To the mixture was added dry benzene (6 ml) and the mixture was kept in refrigerator overnight. The resulting crystals were collected by filtration. Dark-violet needles (24 mg, 98%). M.p. >250 °C. Anal. Calc. for $C_{102}H_{68}B_2F_{48}SRu_2$: C, 49.77; H, 2.78. Found: C, 49.89; H, 3.06%. ^1H NMR (400 MHz, CD_3NO_2): δ 1.94 (s, 30H), 5.02 (m, 2H, η-C_5H_4), 5.44 (m, 2H, η-C_5H_4), 5.79 (m, 2H, η-C_5H_4), 5.85 (m, 2H, η-C_5H_4), 6.29 (m, 2H, =CH), 6.42 (s, 2H, Th-ring), 6.92 (m, 2H, =CH), 7.67 (bs, 8H, Ar–H), 7.84 (bs, 16H, Ar–H).

3.15. Two electron oxidation of *14*

(a) To a solution of **14** (8.0 mg, 0.01 mmol) and *p*-benzoquinone (3 mg, 0.02 mmol) in CH_2Cl_2 (3 ml) was added BF_3OEt_2 (1 drop from a capillary) at 0 °C under nitrogen. The resulting deep blue solution was stirred for 20 min. The deep-blue crystals were resulted in. Addition of dry diethyl ether (4 ml) changed the color of crystals to red violet, and kept for 1 h at 0 °C. Filtration gave black crystalline solids (9.6 mg, 99%).

(b) To a solution of **14** (7.4 mg, 0.01 mmol) and *p*-benzoquinone (2.1 mg, 0.02 mmol) in CH_2Cl_2 (3 ml) was added $Na^+[BAr'_4]^-$ (17.7 mg, 0.02 mmol). The solution was stirred for 2 h at 0 °C under N. Dry benzene (10 ml) was added to the solution twice every 1 h. The resulting crystals were collected by filtration. Deep-violet needles (20 mg, 79%). ^1H NMR spectrum (400 MHz, CD_3NO_2): δ 2.05 (s, 30H), 5.00 (m, 2H, η-C_5H_4), 5.44 (m, 2H, η-C_5H_4), 5.73 (m, 2H, η-C_5H_4), 5.81 (m, 2H, η-C_5H_4), 6.49 (bd, $J = 13$ Hz, 2H, =CH), 6.65 (bd, $J = 13$ Hz, 2H, =CH), 7.13 (s, 2H, Th-ring). The solution was unstable at room temperature.

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