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The synthesis and redox behaviors of binuclear ruthenocene derivatives bridged by an aromatic moiety

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Abstract

2-Ruthenocenyl-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane was prepared by the boration and the subsequent reaction with dilithium pinacolate as the starting material of the Suzuki–Miyaura coupling reaction. The dioxaborolane was heated with 1,4-dibromobenzene, 1,2-diiodobenzene, 4,4′-dibromobiphenyl, 1,4-dibromonaphthalene, and 2,6-dibromonaphthalene in the presence of (dppf)$PdCl_2$–aqueous NaOH in DME to give the corresponding bis(ruthenocenyl) derivatives in moderate yields. The reaction of the dioxaborolane with 2,2′-diiodobiphenyl and 1,8-diiodo-naphthalene in the presence of $Pd(PPh_3)_4$–$Cs_2(CO)_3$ in *N*,*N*-dimethylformamide (DMF) produced ruthenoceno[l]phenanthrene and ruthenocenyl[a]acenaphthylene in low yield, respectively. The result of the cyclic voltammetry suggests that there is weak electronic interaction between the two metal sites in the two-electron oxidized species of the binuclear ruthenocene derivatives with an aromatic bridge.

Keywords: Dioxaborolane; Suzuki–Miyaura coupling reaction; Binuclear ruthenocene derivatives; Redox behavior

1. Introduction

Much attention is focused on bi- and multi-nuclear transition-metal complexes with unsaturated bridges [1], since electronic communication between the metal centers should lead to unusual physical and chemical properties. In particular, the chemistry of binuclear Ru complexes has been investigated well from the viewpoint of their interesting redox properties. Various binuclear acetylide complexes are prepared: the ethynediyl complex, $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C\equiv C)$ [2]; the butadiynediyl complex, $\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C\equiv C)$ [3], $\{Ru(CO)(PPh_3)(dppf)\}_2(C\equiv C-C_6H_4C\equiv C)$ [4], and $\{trans\text{-}RuCl(P-P)\}_2(C\equiv CRC\equiv C)$ (P–P = dppm, dppe, or dmpe; R = 1,4-benzenediyl, 1,3-benzenediyl, 2,5-xylenediyl, 2,5-pyridinediyl, or 2,5-thiophenediyl) [5]. The C_5H_5-bridged dimeric Ru complexes [6], the alkene-bridged Ru complexes [7], the butadiynediyl bridged (β-diketonato)Ru complex were also prepared [8]. The Ru ethynediyl complex, $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C\equiv C)$, was used in the preparation of the four-nuclear cluster [9]. The valence-averaged mixed-valence complex, $[Ru_2(C_{20}H_{36}N_8)Cl_4]^+$, was reported [10]. The oxidative behavior of the binuclear ruthenium complexes is also interesting. The oxidation of [1.1]ruthenocenophane led to the Ru–Ru bond formation [11]. Biruthenocene gave the fulvalene complex having a curious coordination mode in the oxidation [12]. Bis(ruthenocenyl)ethenes cause the structural rearrangement of the complexes having a pentafulvadiene ligand in the 2-electron oxidation [13]. The oxidative cleavage of the S–S bond in bis(ruthenocenyl)disulfide gave the cationic cyclopentadiene-1-thione complex [14]. We now report the synthesis and properties of the binuclear ruthenocene derivatives bridged by an aromatic moiety.

2. Results and discussion

2.1. Synthesis of ruthenocenyldioxaborolane

The cross-coupling reaction is considered to be the best choice for the preparation of binuclear ferrocene derivatives [15], but a similar approach starting with metal-functionalized ruthenocene has been little used. As the only example, the cross-coupling reaction using

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the in situ-prepared chlorozinc derivative was reported in ruthenocene chemistry [16]. Recently, some haloborane derivatives of ruthenocene were reported [17,18]. We selected a dioxaborolane derivative of ruthenocene as the starting material for the preparation of binuclear ruthenocene derivatives. Ruthenocene was heated with one equivalent of boron tribromide in hexane [8] and subsequently treated with dilithium pinacolate in tetrahydrofuran (THF) at 0 °C to give 4,4,5,5-tetramethyl-2-ruthenocenyl-1,3-dioxa-2-borolane (**1**) in 66% yield (Scheme 1). This compound could be separated from the starting material by deactivated alumina. When the intermediate dibromoruthenocenylborane was treated similarly with dilithium 2,3-butanediolate or bis(trimethylsiloxy)ethane, the formation of the corresponding borolane derivatives in the reaction mixture was confirmed by ^{1}H-NMR spectrum, but the product was not isolated because of the easy protodeboration on Al_2O_3 or SiO_2. The ^{1}H-NMR spectrum of **1** showed the methyl protons at δ 1.28 (12H), the protons of unsubstituted (cyclopentadienyl) Cp ring at δ 4.53 and the protons of substituted Cp ring at δ 4.71 (2H) and 4.75 (2H). The structure of **1** was confirmed by the single-crystal X-ray diffraction. The crystallographic data is collected in Table 1 and selected bond distances and angles in Table 2. The ORTEP view of **1** is shown in Fig. 1. In the molecule, there is a symmetry plane bisecting the borolane ring and the two Cp rings of the ruthenocene nucleus through the B(1), C(1), and C(6) atoms. The Cp rings of the ruthenocene nucleus are completely staggered. There is a large disorder in the methyl groups attached to the carbon atoms at 4,5-positions of the dioxaborolane ring. The B−C bond distance [1.537(12) Å] is somewhat shorter than that observed in $PhB(OH)_2$ (1.565 Å) [19] and considerably longer than that in $FcBBr_2$ [1.482(8) and 1.474(9) Å] [20] which is considered to have a pronounced double bond character in the B−C bond [17,18]. Another noticeable point in **1** is the coplanarity (2.37°) between the plane of the dioxaborolane ring and the substituted Cp ring of ruthenocene moiety. These may suggest the presence of the stabilization due to the conjugation of the dioxaborolane ring with ruthenocene.

Table 1
Crystallographic data for **1** and **8**

	1	**8**
Molecular formula	$C_{16}H_{21}BO_2Ru$	$C_{20}H_{14}Ru$
Molecular weight	357.20	718.50
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pmnb*	*P*212121
a (Å)	10.701(2)	7.3260(2)
b (Å)	18.312(3)	8.5590(3)
c (Å)	7.908(1)	22.2240(8)
V (Å^3)	1549.7(4)	1393.52(8)
Z	4	4
Dcalc (g cm^{-3})	1.531	1.694
Crystal size (mm)	0.62 × 0.34 × 0.18	0.35 × 0.08 × 0.08
Radiation (λ, Å)	Mo−K_α (0.71073)	Mo−K_α (0.71073)
Reflection (*hkl*) limits	$0 \le h \le 13$, $-23 \le k \le 0$, $0 \le l \le 10$	$0 \le h \le 7$, $0 \le k \le 10$, $0 \le l \le 7$
Total reflections measured	2137	2825
Unique reflections	1707	2771
Linear absolute coefficients (cm^{-1})	9.891	3.807
Reflections used in L.S.	1682	2771
L.S. parameters	120	190
R	0.050	0.031
R_w	0.060	0.103
S	2.332	1.557
Maximum peak in final Fourier map, e Å^{-3}	1.35	0.53
Minimum peak in final Fourier map, e Å^{-3}	−0.87	−1.12

Table 2
Selected bond distances (Å) and bond angles (°) for **1**

Bond distances			
C(1)−B(1)	1.537(12)	B(1)−O(1)	1.364(16)
C(7)−O(1)	2.344(9)	C(7)−C(8)	1.45(3)
C(7)−C(9)	1.38(3)	Ru(1)−C(Cp)	2.176(av.)
C(Cp)−C(Cp)	1.428(av.)		
Bond angles			
C(1)−B(1)−O(1)	123.1(11)	O(1)−B(1)−O(1)	113.8(7)
B(1)−C(1)−C(2)	125.9(8)	B(1)−O(1)−C(7)	107.1(7)
C(7)−C(7)−O(1)	1106.0(6)		

2.2. *Cross-coupling reaction*

Ferroceneboronic acid [21] and its ester [22] were reported to be a suitable starting material for the Suzuki−Miyaura coupling reaction with aromatic halides [23]. Compound **1** also carried successfully out the cross-coupling with aromatic halides in a DME−aqueous NaOH mixture, using $PdCl_2$(dppf) as catalyst, as shown by Knapp and Rehahn [21]. Thus, the reaction of **1** with 1,4-dibromobenzene and 1,2-diiodobenzene afforded 1,4-bis(ruthenocenyl)benzene (**2**) and 1,2-bis(ruthenocenyl)benzene (**3**) in 71 and 53% yields, respectively (Scheme 2). Compound **3** was also obtained from **1** and 1,2-diiodobenzene in 42% yield in the non-aqueous conditions using $Pd(PPh_3)_4$ as catalyst in *N*,*N*-dimethylformamide (DMF) [24]. 4,4′-Dibromobiphenyl reacted with **1** to give 4,4′-bis(ruthenocenyl)biphenyl (**4**) in 48% yield. The structure of these compounds was identified by the ^{1}H- and ^{13}C-NMR spectra, mass spectra, and elemental analysis. However, the cross-coupling of 2,2′-dibromo- and 2,2′-diiodobiphenyl with borolane **1** gave no desired product in the aqueous conditions. The similar reaction of **1** with 2,2′-dibromobiphenyl using $Pd(OAc)_2$−P(*o*-biphenyl)(t-Bu)$_2$ as a catalyst [25], which was possible to carry out the

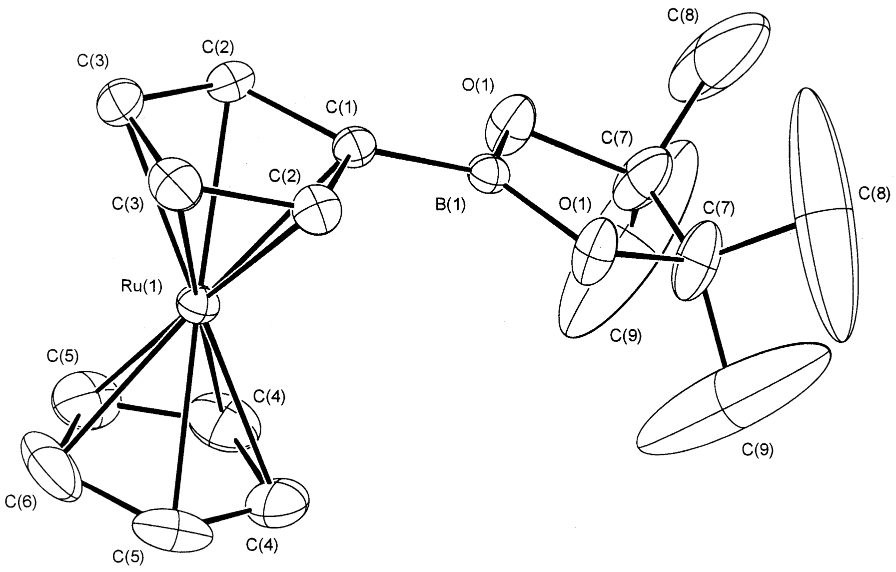


Fig. 1. ORTEP view of **1**.

Suzuki–Miyaura coupling at room temperature, was also unsuccessful. This may be probably because of the increasing steric hindrance in 2,2′-dihalobiphenyl compared with 4,4′-dihalobiphenyl. A similar steric retardation has been observed in the Suzuki–Miyaura coupling reaction to form very hindered biphenyls from aryl halides [26]. 1,4-Bis(ruthenocenyl)naphthalenes (**5**) and 2,6-bis(ruthenocenyl)naphthalenes (**6**) were obtained in 50 and 31% yields by reaction of **1** with the corresponding dibromo derivatives under the conditions using $PdCl_2(dppf)$ as catalyst, respectively. However, 1,8-bis(ruthenocenyl)naphthalene was never produced in the reaction of **1** with 1,8-diiodonaphthalene in similar conditions. This is also due to a large steric hindrance in the product. These results are in contrast to Negishi's coupling using ferrocenylzinc chloride which afforded 2,2′-bis(ferrocenyl)-biphenyl [27] and 1,8-bis(methallocenyl)naphthalene [28].

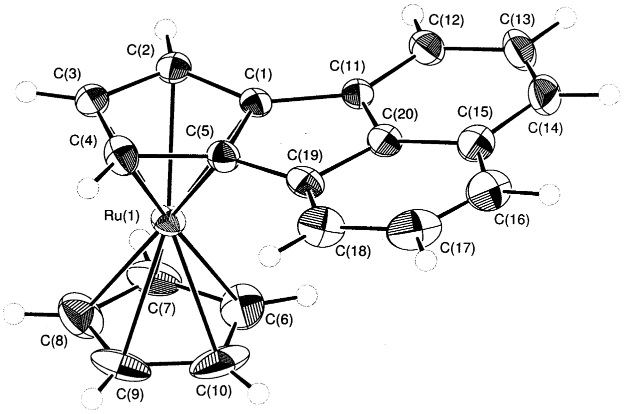


Fig. 2. ORTEP view of **8**.

The cross-coupling reaction of **1** with sterically hindered dihalo aromatics under non-aqueous conditions using $Pd(PPh_3)_4$ led to a considerably different result. The reaction of **1** with 2,2′-diiodobiphenyl in the non-aqueous conditions using $Pd(PPh_3)_4$ as catalyst in DMF [24] gave ruthenocene as a main product and a mononuclear ruthenocene derivative, ruthenoceno[l]phenanthrene (**7**), in very low yield, but not desired binuclear complex, 2,2′-bis(ruthenocenyl)biphenyl (Scheme 3). The structure of **7** can be assigned by the following spectral data: The ^{1}H-NMR spectrum of **7** showed the substituted Cp-ring protons at δ 4.84 (1H) as a triplet and 5.60 (2H) as a doublet, meaning that the

Table 3
Selected bond distances (Å) and bond angles (°) for **8**

Bond distances			
Ru(1)–C(1)	2.207(5)	Ru(1)–C(2)	2.205(6)
Ru(1)–C(3)	2.183(6)	Ru(1)–C(4)	2.191(5)
Ru(1)–C(5)	2.198(6)	C(1)–C(2)	1.433(8)
C(1)–C(5)	1.437(8)	C(2)–C(3)	1.429(7)
C(3)–C(4)	1.432(9)	C(4)–C(5)	1.430(8)
Fe(1)–C(C_5H_5)	2.186(av.)	C(C_5H_5)–C(C_5H_5)	1.40(av.)
C(1)–C(11)	1.454(8)	C(5)–C(19)	1.459(8)
C(11)–C(12)	1.380(8)	C(11)–C(20)	1.421(8)
C(12)–C(13)	1.415(9)	C(13)–C(14)	1.370(9)
C(14)–C(15)	1.427(9)	C(15)–C(20)	1.389(8)
C(15)–C(16)	1.416(9)	C(16)–C(17)	1.36(1)
C(17)–C(18)	1.411(10)	C(18)–C(19)	1.370(8)
C(19)–C(20)	1.438(8)		
Bond angles			
C(1)–C(5)–C(19)	108.4(5)	C(5)–C(1)–C(11)	108.8(5)
C(1)–C(11)–C(20)	105.7(5)	C(5)–C(19)–C(20)	105.2(5)
C(11)–C(20)–C(19)	111.8(5)	C(2)–C(1)–C(5)	108.1(5)
C(1)–C(5)–C(4)	108.5(5)	C(12)–C(11)–C(20)	118.1(6)
C(18)–C(19)–C(20)	117.7(6)	C(11)–C(20)–C(15)	124.5(6)
C(15)–C(20)–C(19)	123.7(6)		

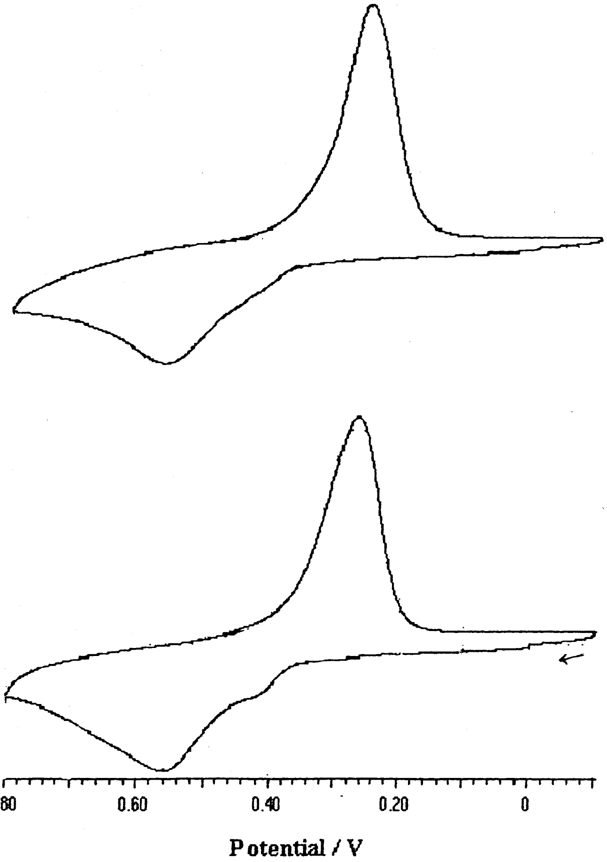


Fig. 3. Cyclic voltammograms of **4** (upper) and **6** (lower).

Cp ring is di-substituted at 1,2-positions by the same substituent. The aromatic ring protons appeared at δ 7.42 (m, 4H), 7.86 (m, 2H), and 8.33 (m, 2H), indicating a symmetrical substitution of the benzene ring. In coincidence with this, the ^{13}C-NMR spectrum of **7** gave only six aromatic carbon signals at δ 123.42, 123.69, 125.61, 127.18, 129.35, and 133.10, along with the ruthenocenyl ring carbon signals at δ 65.49, 71.14, 71.44, and 85.17. The mass spectrum of **12** showed the molecular ion at *m*/*z* 381. The reaction of **1** with 1,8-diiodo-naphthalene in the similar non-aqueous conditions also gave a mononuclear ruthenocene derivative, ruthenoceno[a]acenaphthylene (**8**), in very low yield, along with a large amount of ruthenocene, but no 1,8-bis(ruthenocenyl)naphthalene. The structure of **8** was confirmed by X-ray diffraction. The crystallographic data of **8** are collected in Table 1 and the selected bond distances and angles are collected in Table 3. The ORTEP view of **8** is shown in Fig. 2. Two Cp rings of the ruthenocene moiety adopt an eclipsed form. The ruthenocene is fused with acenaphthylene at the 1,2-positions. The plane of acenaphthylene is inclined by 12° to the outer side of the Cp ring of ruthenocene. The C–C (av. 1.432 Å) and Fe–C bond distances (av. 2.197 Å) of the substituted Cp ring in the ruthenocene moiety are similar to those of ruthenocene itself, indicating no strain due to the fusion of acenaphthylene in the ruthenocene moiety. The normal bond alternation observed in the naphthalene ring of **8** means little strain in the naphthalene ring, but the six-membered ring of naphthalene is somewhat distorted because of the fusion of a five-membered ring in the *peri*-positions [e.g. C(12)–C(11)–C(20) 118.1(6)° and C(11)–C(20)–C(15) 124.5(6)°].

Table 4
The oxidation potentials (*V* vs. FcH–FcH$^+$) of compounds **1**–**6**

Compound	$E_{pa}(1)$	$E_{pa}(2)$
RcH		0.53
1		0.55
2	0.42	0.46
3		0.52
4	0.32(sh)	0.43
5		0.49
6	0.28(sh)	0.42

2.3. Redox property

The cyclic voltammograms of compounds **1**–**6** and ruthenocene were measured in a solution of 0.1 M *n*-Bu_4NClO_4 in CH_2Cl_2 at a glassy carbon (GC) electrode and a sweep rate of 0.1 V s^{-1}. The oxidation and reduction potentials are summarized in Table 4. Binuclear ruthenocene compounds, **2**, **4**, and **6**, showed a broad irreversible oxidation wave near 0.5 V and a shoulder near 0.3 V, as exemplified in Fig. 3. The large wave near 0.5 V is assigned to be due to the superimposed two one-electron oxidation [Ru(II)–Ru(III) and Ru(III)–Ru(IV)] of two ruthenocenyl nuclei, in comparison with that of ruthenocene. The latter shoulder seems to be caused by the superimposed one-electron oxidation [Ru(II)–Ru(III)] of two ruthenocenyl nuclei, since 1,2-bis(ruthenocenyl)- and *trans*-1,2-dimethyl-1,2-bis(ruthenocenyl)ethenes, in which a strong electronic interaction between the metal sites was observed in their two-electron oxidized species, exhibited the two-electron redox wave at lower potential, 0.03 and 0.18 V, respectively [13]. The appearance of the two-electron oxidation wave as a shoulder suggests that the two-electron oxidized species of these compounds are stable to some extent. That is, there would be probably a little electronic communication through the aromatic ring between two ruthenocenyl nuclei in the two-electron oxidized species of **2**, **4**, and **6**. On the other hand, compounds, **3** and **5**, showed no shoulder near 0.3 V, likely indicating no stabilization of the two-electron oxidized species. In compound **3**, the two ruthenocenyl nuclei seem to be not coplanar with the benzene ring as a result of the steric hindrance in the benzene ring *ortho*-disubstituted by ruthenocene, similar to that shown in the X-ray analysis of 1,2-bis(ferrocenyl)benzene [22].

Also, the two substituted Cp rings in the ruthenocenyl nuclei of **5** are not coplanar with the naphthalene ring because of the steric hindrance by the *peri*-hydrogen atom of naphthalene. As a result, the electronic communication between the two ruthenocenyl nuclei in **3** and **5** may be greatly disturbed in the two-electron oxidized species. Thus, the data obtained from the CV (cyclic voltammetric) measurement of **2**–**6** may be able to estimate the electronic interaction between the Ru sites in the two-electron oxidized species of the binuclear ruthenocenes bridged by aromatic moieties, if we can assume that the magnitude of the oxidation wave near 0.3 V is parallel to that of the electronic interaction between the metal sites. Thus, the electronic interaction in the two-electron oxidized species of the naphthalene derivative (**6**) is inferred to be somewhat larger than that of benzene derivatives (**2**). The aromatics-bridged biruthenocene derivatives showed weak electronic interaction in the two-electron oxidized species as described above, while a significant electronic interaction was observed for the bis(ruthenocenyl)ethenes [13]. Therefore, the former small interaction is probably because the interaction between the metal sites is cross-conjugated with the aromaticity of the bridge in former compounds. The fact that the electronic interaction in the two-electron oxidized species of **6** is somewhat larger than that of **2** probably may reflect the strength of aromaticity: benzene > naphthalene.

2.4. Chemical oxidation

The increased electronic interaction between the two Ru sites may indicate the increased stability in the two-electron oxidized species of the binuclear ruthenocenes. So, compound **6**, bridged by naphthalene at 2,6-positions and exhibiting the largest shoulder near 0.3 V among the binuclear ruthenocenes bridged by aromatics, was oxidized with two equivalents of *para*-benzoquinone and $BF_3 \cdot OEt_2$ in CH_2Cl_2 at 0 °C. The resulting dark violet precipitate, which may be considered to be the two-electron oxidized species, was obtained. However, it was unstable and gave no definite ^{1}H-NMR signal when it was dissolved in CD_3NO_2 or CD_3CN.

3. Conclusion

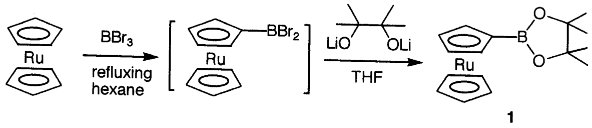
The binuclear ruthenocene derivatives bridged by phenylene, biphenylene, and naphthalenylene were synthesized using Suzuki–Miyaura cross-coupling reaction of ruthenocenyl–dioxaborolane, newly prepared. The compounds showed no distinct oxidation wave at lower potential in their cyclic voltammograms, indicating weak electronic communication between the two ruthenocenyl nuclei in the two-electron oxidized species. In the case of 2,2′-diiodobiphenyl and 1,8-diiodonaphthalene, unusual products, ruthenoceno[l]phenanthrene and ruthenoceno[a]acenaphthylene, were obtained, although in low yields, respectively.

4. Experimental

All reactions were carried out under an atmosphere of N_2 and/or Ar, and work-ups were performed without precaution to exclude air. NMR spectra were recorded on BRUKER AM400, ARX400, AC300P, or AC200 spectrometer. IR (KBr disc) spectra were recorded on Perkin–Elmer System 2000 spectrometer. CV was carried out by using ALS 600 in 10^{-1} M solution of n-Bu_4NClO_4 (polarography grade, Nacalai tesque) in CH_2Cl_2. CV's cells were fitted with GC working electrode, Pt wire counter electrode and Ag–Ag^+ pseudo reference electrode. The cyclic voltammograms were obtained at the scan rate of 0.1 V s^{-1} in the 10^{-3} M or saturated solution of complexes. All potentials were represented versus FcH–FcH^+, which were obtained by the subsequent measurement of ferrocene at the same conditions. THF was purified by distillation from the drying agent, Na–benzophenone. Ruthenocene was prepared according to the literature [29]. Other reagents were used as received from commercial suppliers.

4.1. 2-Ruthenocenyl-1,3-dioxa-2-borolane (*1*)

To a suspension of ruthenocene (2.00 g, 8.65 mmol) in hexane (65 ml) tribromoborane (10.4 ml, 10.4 mmol) was drop-wise added under nitrogen. The mixture was refluxed for 1 h. The resulting light brown solution was cooled to room temperature and drop-wise added at 0 °C to a solution of dilithium pinacolate which was prepared from pinacol (1.35 g, 11.4 mmol) and n-BuLi (16.5 ml of 1.5 M solution in hexane, 25.2 mmol) in THF (150 ml) at 0 °C. After stirring for 10 min at 0 °C, the solvent was evaporated under vacuum. The residue was dissolved in benzene (100 ml). The solution was washed with saturated solution of NH_4Cl in water and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on deactivated Al_2O_3 with 5% H_2O by elution of benzene–EtOAc (1:1). Recrystallization from hexane gave yellow crystals (2.04 g, 66%). Melting point (m.p.) 144 °C. Found: C, 53.94; H, 5.96%. Anal. Calc. for $C_{16}H_{21}O_2BRu$: C, 53.80; H, 5.93%. ^{1}H-NMR ($CDCl_3$): δ 1.28 (s, 12H, CH_3), 4.53 (s,



Scheme 1.

5H, η-C_5H_5), 4.71 (t, 2H, $J=2$ Hz, η-C_5H_4), and 4.75 (t, 2H, $J=2$ Hz, η-C_5H_4). ^{13}C-NMR ($CDCl_3$): δ 24.59 (CH_3), 70.57 (C + η-C_5H_4), 73.38 (η-C_5H_5), 74.97 (η-C_5H_4), and 82.99 (*ipso*-η-C_5H_4).

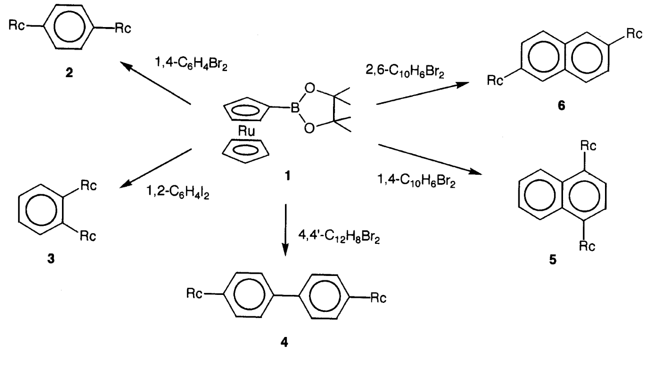
*4.2. 1,4-Bis(ruthenocenyl)benzene (**2**)*

4.2.1. General procedure

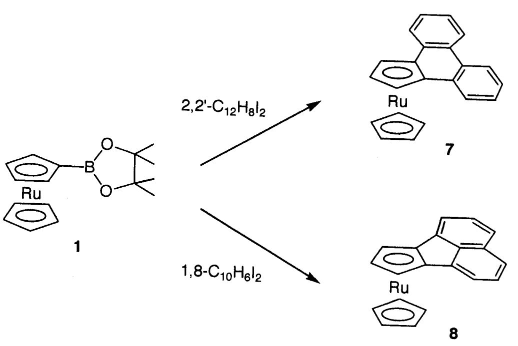
A mixture of **1** (0.34 g, 0.96 mmol), 1,4-dibromobenzene (94 mg, 0.4 mmol), $PdCl_2$(dppf) (11 mg, 0.013 mmol), 3 M aqueous solution of NaOH (3 ml), and DME (3 ml) was heated for 48 h at 120 °C under Ar in a sealed tube. After cooling, the mixture was dissolved in CH_2Cl_2. The organic layer was separated, washed with water, and then dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 by elution of benzene to give yellow crystals, along with ruthenocene (90 mg, 41%). The crystals were recrystallized from benzene–hexane to give pale yellow crystals (152 mg, 71%), m.p. > 250 °C. Found: C, 58.54; H, 4.12%. Anal. Calc. for $C_{26}H_{22}Ru_2$: C, 58.20; H, 4.13%. MS (EI, 70 eV): *m/z* 536 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 4.47 (s, 10H, η-C_5H_5), 4.64 (t, 4H, $J=2$ Hz, η-C_5H_4), 5.00 (t, 4H, $J=2$ Hz, η-C_5H_4), and 7.24 (s, 4H, C_6H_4). ^{13}C-NMR ($CDCl_3$): δ 69.37 (η-C_5H_4), 70.67 (η-C_5H_5), 71.39 (η-C_5H_4), 90.23 (*ipso*-η-C_5H_4), 126.34 (C_6H_4) and 136.19 (*ipso*-C_6H_4).

*4.3. 1,2-Bis(ruthenocenyl)benzene (**3**)*

This compound was prepared from **1** (0.34 g, 0.96 mmol) and 1,2-diiodobenzene (132 mg, 0.4 mmol). The product was recrystallized from $CHCl_3$–hexane. Pale yellow crystals (112 mg, 53%), m.p. 224 °C (dec.). Found: C, 53.26; H, 3.71%. Anal. Calc. for $C_{26}H_{22}Ru_2CHCl_3$: C, 53.38; H, 3.80%. ^{1}H-NMR ($CDCl_3$): δ 4.50 (s, 10H, η-C_5H_5), 4.52 (t, 4H, $J=2$ Hz, η-C_5H_4), 4.60 (t, 4H, $J=2$ Hz, η-C_5H_4), 7.08 (q, $J=3$ Hz, 2H, C_6H_4), and 7.42 (q, $J=3$ Hz, 2H, C_6H_4). ^{13}C-NMR ($CDCl_3$): δ 69.57 (η-C_5H_4), 71.35 (η-C_5H_5), 73.72 (η-C_5H_4), 93.34 (*ipso*-η-C_5H_4), 125.86 (C_6H_4), 132.37 (C_6H_4), and 136.37 (*ipso*-C_6H_4).



Scheme 2.



Scheme 3.

*4.4. 4,4′-Bis(ruthenocenyl)biphenyl (**4**)*

This compound was prepared from **1** (0.36 g, 1.0 mmol) and 4,4′-dibromobiphenyl (125 mg, 0.40 mmol). Pale yellow crystals (103 mg, 43%), m.p. > 260 °C. Found: C, 62.70; H, 4.21%. Anal. Calc. for $C_{32}H_{26}Ru_2$: C, 62.73; H, 4.28%. ^{1}H-NMR ($CDCl_3$): δ 4.50 (s, 10H, η-C_5H_5), 4.68 (t, 4H, $J=1.6$ Hz, η-C_5H_4), 5.06 (t, 4H, $J=1.6$ Hz, η-C_5H_4), and 7.45 (m, 8H, $C_{12}H_8$). ^{13}C-NMR ($CDCl_3$): δ 69.57 (η-C_5H_4), 71.35 (η-C_5H_5), 73.72 (η-C_5H_4), 93.34 (*ipso*-η-C_5H_4), 125.86 (C_6H_4), 132.37 (C_6H_4), and 136.37 (*ipso*-C_6H_4).

*4.5. 1,4-Bis(ruthenocenyl)naphthalene (**5**)*

This compound was prepared from **1** (0.36 g, 1.0 mmol) and 1,4-dibromonaphthalene (114 mg, 0.40 mmol). Pale yellow crystals (115 mg, 50%), m.p. 200–201 °C. Found: C, 61.32; H, 4.04%. Anal. Calc. for $C_{30}H_{24}Ru_2$: C, 61.42; H, 4.12%. ^{1}H-NMR ($CDCl_3$): δ 4.63 (s, 10H, η-C_5H_5), 4.73 (t, 4H, $J=1.5$ Hz, η-C_5H_4), 4.97 (t, 4H, $J=1.5$ Hz, η-C_5H_4), 7.43 (m, 2H, 6,7-H), 7.60 (s, 2H, 2,3-H), and 8.50 (m, 2H, 5,8-H). ^{13}C-NMR ($CDCl_3$): δ 70.21 (η-C_5H_4), 71.55 (η-C_5H_5), 73.41 (η-C_5H_4), 92.36 (*ipso*-η-C_5H_4), 125.00 ($C_{10}H_6$), 126.58 ($C_{10}H_6$), 128.56 ($C_{10}H_6$), 132.08 (q-$C_{10}H_6$), and 133.90 (q-$C_{10}H_6$).

*4.6. 2,6-Bis(ruthenocenyl)naphthalene (**6**)*

This compound was prepared from **1** (0.36 g, 1.0 mmol) and 2,6-dibromonaphthalene (114 mg, 0.40 mmol). Pale yellow crystals (68 mg, 29%), m.p. 200–200.5 °C. Found: C, 61.24; H, 4.10%. Anal. Calc. for $C_{30}H_{24}Ru_2$: C, 61.42; H, 4.12%. ^{1}H-NMR ($CDCl_3$): δ 4.48 (s, 10H, η-C_5H_5), 4.71 (t, 4H, $J=1.5$ Hz, η-C_5H_4), 5.14 (t, 4H, $J=1.5$ Hz, η-C_5H_4), 7.37 (d, 2H, $J=8.5$ Hz, 3,7-H), 7.62 (d, 2H, $J=8.5$ Hz, 4,8-H), and 7.88 (s, 2H, 1,5-H). ^{13}C-NMR ($CDCl_3$): δ 69.45 (η-C_5H_4), 70.98 (η-C_5H_4), 71.44 (η-C_5H_5), 90.09 (*ipso*-η-C_5H_4), 123.64 ($C_{10}H_6$), 126.04 ($C_{10}H_6$), 127.18 ($C_{10}H_6$), 132.17 (q-$C_{10}H_6$), and 135.36 (q-$C_{10}H_6$).

4.7. Ruthenocenyl[l]phenanthrene (**12**)

After a solution of **1** (0.26 g, 0.7 mmol), 2,2′-diiodobiphenyl (122 mg, 0.3 mmol) in dimethylformamide (2.5 ml) was bubbled with nitrogen for 20 min, $Pd(PPh_3)_4$ (12 mg) and $Cs_2(CO)_3$ (0.23 g, 0.7 mmol) were added, and the mixture was heated at 90 °C for 4 h under Ar. The mixture was diluted with benzene (30 ml), and the solution was washed with water (40 ml) twice and then conc. aqueous LiCl (20 ml) twice. After being dried with $MgSO_4$, the solution was evaporated by evaporator. The residue was chromatographed on SiO_2 by elution of hexane–benzene (3:1) to give **12** (11 mg, 3%) as yellow crystals, along with ruthenocene (0.18 g, 80%). M.p. 183–184 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.14 (s, 5H, η-C_5H_5), 4.84 (t, $J = 2.4$ Hz, 1H, η-C_5H_4), 5.60 (d, $J = 2.4$ Hz, 2H, η-C_5H_4), 7.42 (m, 4H, 2,3,7,8-H), 7.86 (m, 2H, 1,8-H), 8.33 (m, 2H, 4,5-H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 65.49 (η-C_5H_4), 71.14 (η-C_5H_4), 71.44 (η-C_5H_5), 85.17 (*ipso*-η-C_5H_4), 123.42 ($C_{12}H_8$), 123.69 ($C_{12}H_8$), 125.61 ($C_{12}H_8$), 127.18 ($C_{12}H_8$), 129.35 (q-$C_{12}H_8$), 133.10 (q-$C_{12}H_8$). MS (EI, 75 eV): *m/z* 381 [M^+].

4.8. Ruthenoceno[a]acenaphthylene (**13**)

This compound was obtained from the reaction of **1** with 1,8-diiodonaphthalene under the same conditions used in the reaction of **1** with 2,2′-diiodobiphenyl described above. Yield: 13 mg (3%). Yellow needles. M.p. 166–167 °C. Found: C, 67.47; H, 3.88%. Anal. Calc. for $C_{20}H_{14}Ru$: C, 67.59; H, 3.97%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.30 (s, 5H, η-C_5H_5), 4.80 (t, $J = 2.2$ Hz, 1H, η-C_5H_4), 5.20 (d, $J = 2.2$ Hz, 2H, η-C_5H_4), 7,36 (dd, $J = 7.0$ and 8.1 Hz, 4H, 4,7-H), 7.50 (dd, $J = 7.0$ and 0.7 Hz, 2H, 3,8-H), 7.59 (dd, $J = 8.1$ and 0.7 Hz, 2H, 5,6-H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 65.49 (η-C_5H_4), 71.14 (η-C_5H_4), 71.44 (η-C_5H_5), 85.17 (*ipso*-η-C_5H_4), 123.42 ($C_{12}H_8$), 123.69 ($C_{12}H_8$), 125.61 ($C_{12}H_8$), 127.18 ($C_{12}H_8$), 129.35 (q-$C_{12}H_8$), 133.10 (q-$C_{12}H_8$). MS (EI, 75 eV): *m/z* 355 [M^+].

4.9. Structure determination

The crystallographic data for complexes **1** and **8** are summarized in Table 1. In complex **1**, data collection was performed at room temperature on Mac Science MXC18K diffractometer with graphite monochromated Mo–K_α radiation and an 18 kW rotating anode generator. In complex **8**, oscillation and non-screen Weissenberg photographs were recorded on the imaging plates on Mac Science DIP3000 diffractometer with graphite monochromated Mo–K_α radiation and an 18 kW rotating anode generator. The data reduction and determination of cell parameters were made by the MAC DENZO program system. The structures were solved by the SIR 92 method in CRYSTAN-GM (software-package for structure determination) for **1** and the SIR 92 in MAXUS (software-package for structure determination) for **8** and refined by full-matrix least-squares procedure. Anisotropic refinements for non-hydrogen atom were carried out. All the hydrogen atoms, partially located from differential Fourier map, for complex **8** were isotropically refined. In complex **1**, no hydrogen was located.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178850 for complex **1** and CCDC no. 178851 for complex **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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