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Synthesis, structure and redox chemistry of 1,2-bis(ruthenocenyl)ethylene derivatives: a novel structural rearrangement to a (μ-η^6 : η^6-pentafulvadiene)diruthenium complex upon two-electron oxidation†

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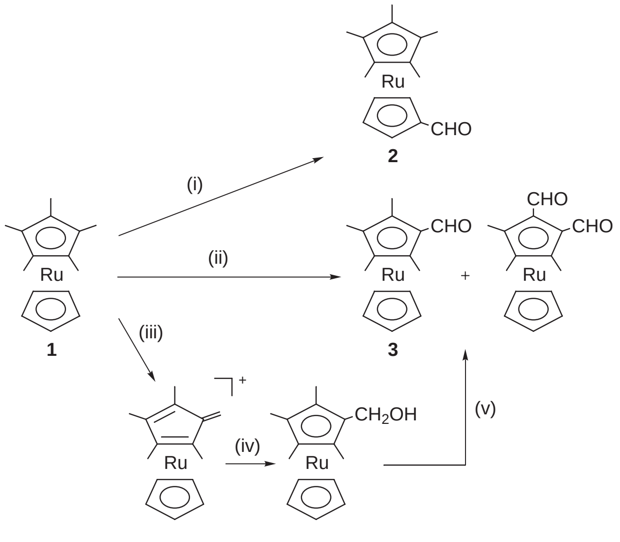
Formylruthenocene, 1-formyl-1′,2′,3′,4′,5′-pentamethylruthenocene and 1-formyl-2,3,4,5-tetramethylruthenocene were treated with $TiCl_4$–Zn in thf to afford the corresponding ethylene derivatives *trans*-1,2-bis(ruthenocenyl)ethylene, *trans*-1,2-bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethylene and *trans*-1,2-bis(2,3,4,5-tetramethylruthenocenyl)ethylene in excellent yields. Similarly, the dimethyl analogs were obtained from acetylruthenocene and 1-acetyl-1′,2′,3′,4′,5′-pentamethylruthenocene in good yields. Cyclic voltammograms of the ethylene complexes showed an irreversible two-electron oxidation wave at significantly lower potential than that of pentamethylruthenocene or ruthenocene. Two-electron chemical oxidation of these complexes with *p*-benzoquinone–$BF_3{\cdot}OEt_2$ gave stable dicationic (μ-η^6 : η^6-pentafulvadiene)diruthenium complexes in moderate yields. The molecular structures of five complexes were determined by X-ray diffraction.

Redox active binuclear organometallic complexes with a conjugated hydrocarbon bridging ligand, corresponding to organometallic versions of the multistage redox systems first described by Deuchert and Hünig,[1] have attracted much attention in both fundamental and applied studies.[2–7] A large number of dinuclear complexes with conjugated bridges have been reported, of which the chemistry of bis(ferrocenyl) compounds has been well investigated, particularly from the viewpoint of mixed valence, because ferrocene has a well defined and stable one-electron redox system.[8] Ferrocene has also been recognized as a good trigger and termini for electronic switching phenomena.[9] Ruthenocene is a stable metallocene similar to ferrocene but shows different electochemical properties.[10] Owing to its irreversible two-electron oxidation process, there have been few reports about bis(ruthenocenyl) compounds.[11–15]

We have focused on redox-active heterobinuclear complexes (hetero species and/or co-ordination environment) including ferrocene or ruthenocene as part of the redox centers and investigated the electronic structures of the mixed-valence states,[16a–e] and the novel reactions[16d,f] and the structural rearrangement[17] upon one- or two-electron oxidation. The ruthenocene moiety in the ruthenium(II) ruthenocenylacetylide complexes showed a reversible one-electron oxidation process in the cyclic voltammogram and transformed into a fulvene-like complex upon two-electron oxidation.[17] These findings stimulated us to investigate in detail the electronic structure of bis(ruthenocenyl) compounds connected by a conjugated hydrocarbon bridge in order to elucidate the electrochemical behaviour of the ruthenocene moiety and the metal–metal interaction. We here report the synthesis, structure and redox chemistry of 1,2-bis(ruthenocenyl)ethylene derivatives and oxidatively induced structural rearrangement to the unprecedented stable dicationic (μ-η^6 : η^6-pentafulvadiene)diruthenium complexes.[15]



Scheme 1 (i) $POCl_3$–dmf, $(CH_2Cl)_2$; (ii) activated MnO_2, $(CH_2Cl)_2$; (iii) *p*-benzoquinone (2 equivalents)–$BF_3{\cdot}OEt_2$ (10 equivalents), CH_2Cl_2; (iv) 10% aqueous KOH, thf; (v) activated MnO_2, $(CH_2Cl)_2$

Results and Discussion

1,2,3,4,5-Pentamethylruthenocene **1** reacted with dmf and $POCl_3$ (Vilsmeier's complex) in 1,2-dichloroethane on reflux for 12 h to give 1-formyl-1′,2′,3′,4′,5′-pentamethylruthenocene **2** in 87% yield. Complex **1** was oxidized with activated MnO_2 in refluxing 1,2-dichloroethane to afford 1-formyl-2,3,4,5-tetramethylruthenocene **3** and 1,2-diformyl-3,4,5-trimethylruthenocene in 37 and 7% yield, respectively, along with the starting material **1** in 40% yield. In another route, the tetramethylfulvene complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_5Me_4CH_2)]^+BF_4^-$, prepared in quantitative yield by the two-electron oxidation of **1** by *p*-benzoquinone–$BF_3{\cdot}Et_2O$,[16] was treated with aqueous KOH in thf to afford a corresponding 1-hydroxymethyl-2,3,4,5-tetramethylruthenocene in 73% yield, which was oxidized with

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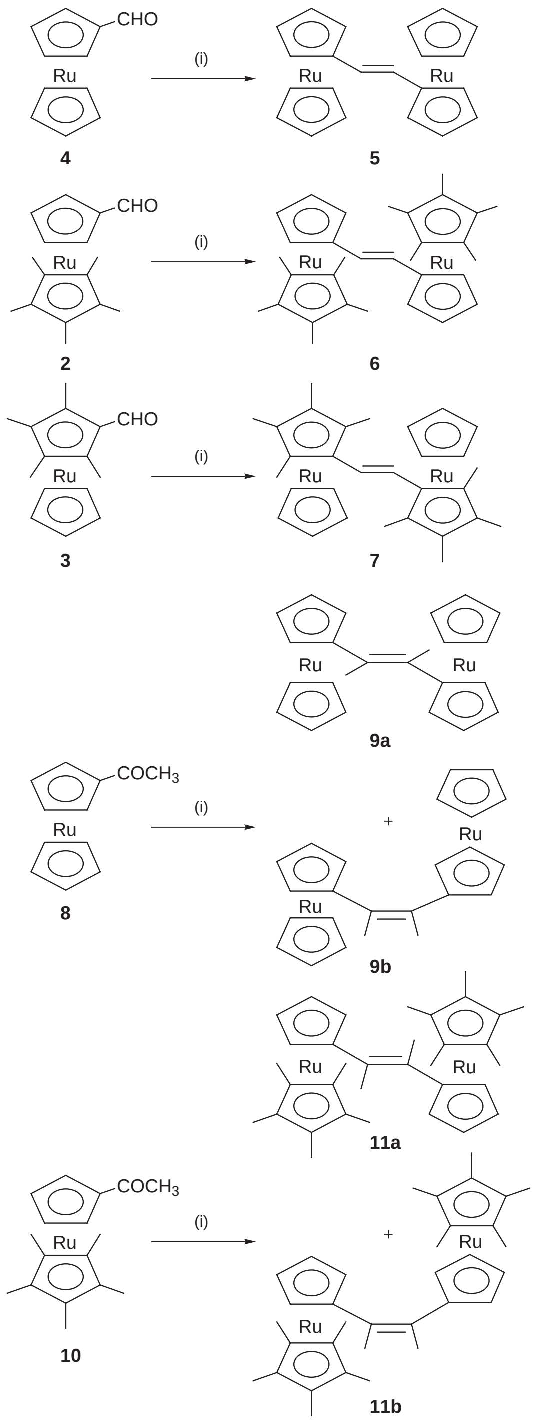
† According to IUPAC nomenclature pentafulvadiene is named 5,5′-(1,2-ethanediylidene)biscyclopenta-1,3-diene. Also, it is called 6,6′-bifulvenyl customarily.



Scheme 2 (i) $TiCl_4$–Zn, thf

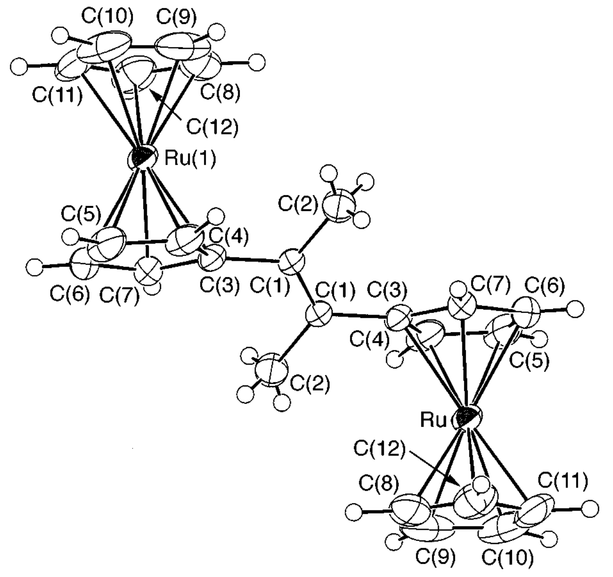


Fig. 1 An ORTEP view of complex **9a**

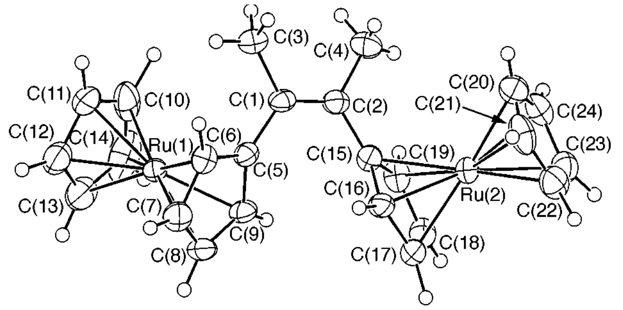


Fig. 2 An ORTEP view of complex **9b**

activated MnO_2 in refluxing 1,2-dichloroethane to give the aldehyde **3**, although in low (24%) yield, along with 1,2-diformyl-3,4,5-trimethylruthenocene in 21% yield (Scheme 1). Formylruthenocene **4** was prepared according to the literature.[18] Complexes **4**, **2** and **3** were treated with low-valent titanium prepared from $TiCl_4$–Zn in thf[19] to afford the corresponding ethylene derivatives, *trans*-1,2-bis(ruthenocenyl)ethylene **5**, *trans*-1,2-bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethylene **6** and *trans*-1,2-bis(2,3,4,5-tetramethylruthenocenyl)ethylene **7**, in 66, 93 and 76% yield, respectively (Scheme 2). The structures of these ethylenes were determined by the spectroscopic data. For example, the strong C=C stretching vibration of **6** was observed at 1646 cm^{-1} in the Raman spectrum. The ^1H NMR spectrum of **6** showed the vinyl proton signal at δ 5.92 and the ^{13}C NMR spectrum exhibited the vinyl carbon signal at δ 121.69. A single crystal X-ray analysis confirmed the *trans* configuration in **6**.[15] Selected bond lengths and angles are summarized in Table 1.

Acetylruthenocene **8** was treated with $TiCl_4$–Zn in thf under gentle refluxing for 2 h to give the coupling products, a mixture of *trans*- (**9a**) and *cis*-1,2-dimethyl-1,2-bis(ruthenocenyl)ethylenes (**9b**) in 83% yield. Similarly, 1-acetyl-1′,2′,3′,4′,5′-pentamethylruthenocene **10** gave *trans*- (**11a**) and *cis*-1,2-dimethyl-1,2-bis(pentamethylruthenocenyl)ethylenes (**11b**) in 70% yield (Scheme 2). These isomers were separated through a fractional recrystallization. In the ^1H NMR spectrum the product **9a** showed the ring protons of the ruthenocenyl moiety at δ 4.55 (10 H), 4.63 (4 H) and 4.54 (4 H), similar chemical shifts to those of the *trans* isomer of the parent 1,2-bis(ruthenocenyl)ethylene **5** [δ 4.49 (10 H), 4.74 (4 H) and 4.55 (4 H)]. On the other hand, the protons of the substituted C_5H_4 rings in **9b** [δ 4.43 (4 H) and 4.40 (4 H)] and the methyl signal (δ 1.84) were at higher field than the corresponding signals of **9a**. The total similarity in the chemical shifts of the ruthenocenyl moiety for **9a** to those for **5** may suggest that **9a** can be assigned to a *trans* isomer. This assignment was confirmed by X-ray diffraction (see below). The proton signals of the C_5H_4 ring of ruthenocene and the methyl group attached to the ethylene carbon for product **11a** [δ 4.35 (4 H), 4.15 (4 H) and 1.98 (6 H), respectively] were at lower field than those for product **11b** [δ 4.06 (4 H), 4.00 (4 H) and 1.86 (6 H), respectively]. From the similarity of the chemical shifts with those for **9a** and **9b** it is suggested that **11a** is a *trans* and **11b** a *cis* isomer.

Single crystals suitable for X-ray diffraction of **9a** and **9b** were obtained by recrystallization from chloroform–diethyl ether using a diffusion method. The ORTEP[20] views are shown in Figs. 1 and 2, respectively. Half of the molecule for **9a** is crystallographically unique, with the whole molecule located on an inversion center. Selected bond distances and angles for **9a** and **9b** are summarized in Table 1. The most significant differ-

Table 1 Selected bond distances (Å) and angles (°) for complexes **6**, **9a** and **9b**

6		**9a**		**9b**	
C(1)–C(1)	1.359*	C(1)–C(1)	1.348(5)	C(1)–C(2)	1.342(9)
C(1)–C(2)	1.547*	C(1)–C(2)	1.498(6)	C(1)–C(3)	1.509(8)
				C(2)–C(4)	1.498(10)
		C(1)–C(3)	1.487(6)	C(1)–C(5)	1.475(9)
				C(2)–C(15)	1.471(9)
Ru(1)–C(ring)	2.18*	Ru(1)–C(ring)	2.174*	Ru(1)–C(ring)	2.174*
C–C(ring)	1.41*	C–C(ring)	1.410*	C–C(ring)	1.418*
C(1)–C(1)–C(2)	114.6*	C(1)–C(1)–C(2)	123.1(4)	C(2)–C(1)–C(3)	121.0(6)
				C(1)–C(2)–C(4)	120.8(6)
C(1)–C(2)–C(3)	120.1*	C(1)–C(1)–C(3)	122.5(4)	C(2)–C(1)–C(5)	124.4(6)
				C(1)–C(2)–C(15)	123.4(6)
		C(2)–C(1)–C(3)	114.4(4)	C(3)–C(1)–C(5)	114.6(5)
				C(4)–C(2)–C(15)	115.8(6)

* Average.

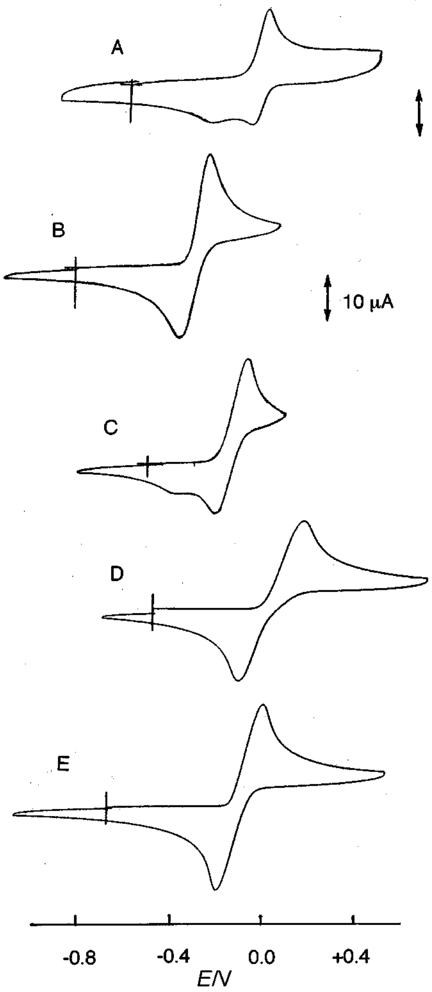


Fig. 3 Cyclic voltammograms of complexes **5** (A), **6** (B), **7** (C), **9a** (D) and **11a** (E) in CH_2Cl_2

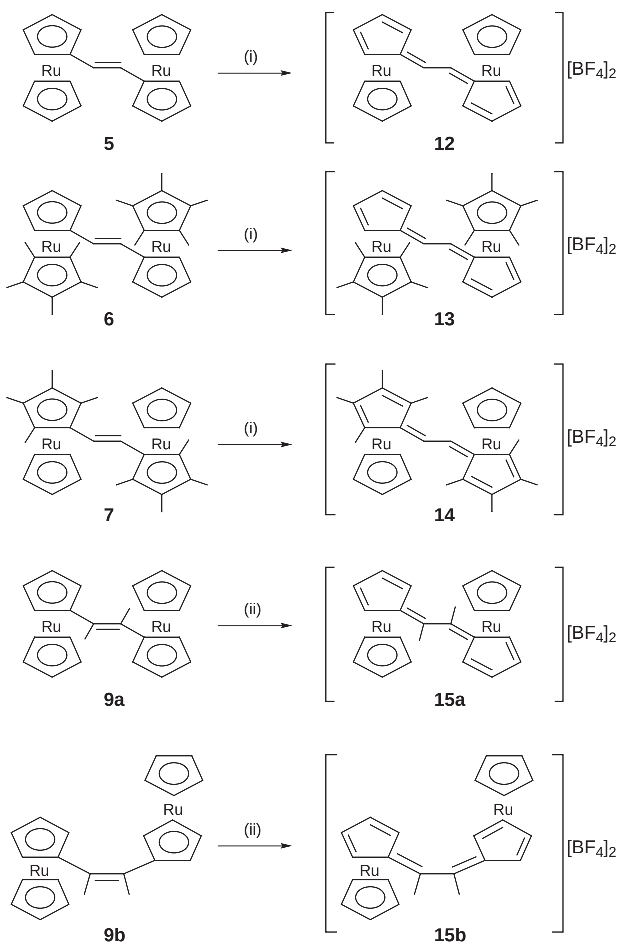
ences of **9a** compared with complex **6** are the fact that the plane of the substituted C_5H_4 ring of the ruthenocene moiety is inclined by 37.27(2)° towards the plane of the ethylene bond, probably because of the steric crowding of the methyl group on the ethylene bond, while the corresponding two planes in **6** are almost coplanar (1.22°). Similarly the plane of the substituted C_5H_4 ring attached to the double bond in the *cis* isomer **9b** inclines by 30.80(3) and 49.89(3)° in order to avoid the steric repulsion between the methyl group on the ethylene and the hydrogen atom on the substituted C_5H_4 ring. The C–C and Ru–C distances of the ruthenocene parts in **9a** and **9b** are normal.

Table 2 Redox potentials of bis(ruthenocenyl)ethylenes and related compounds[a]

Complex	E_{pa}[b]	$E_{pc}(1)$	$E_{pc}(2)$
1	+0.33	—	—
[Ru(η^5-C_5H_5)$_2$]	+0.55	—	—
5	+0.03	−0.03[c]	−0.20[c]
6	−0.19	−0.40[b]	—
7	−0.10	−0.17[c]	−0.27[c]
9a	+0.18	−0.09[b]	—
9b	+0.22	−0.09[c]	—
11a	+0.01	−0.19[b]	—
11b	−0.01	−0.19[b]	—

[a] In V *vs.* ferrocene–ferrocenium. [b] Two-electron process. [c] The process involved less than two electrons.

The cyclic voltammograms of 1,2-bis(ruthenocenyl)ethylenes **5**–**7**, **9** and **11** in CH_2Cl_2 are shown in Fig. 3. The corresponding redox potentials and those of related compounds are summarized in Table 2. For complexes **6**, **9** and **11** an irreversible oxidation wave, confirmed as corresponding to a two-electron process by using the Randles–Sevcik equation and, on the backward scan, an irreversible two-electron reduction wave having nearly the same magnitude as that of the oxidation wave were observed. On the other hand, **5** and **7** showed a quasi-reversible two-electron wave ($E_{pc} - E_{pa} = 0.06$ and 0.07 V, respectively) and small irreversible reduction wave. The difference in redox behavior among **5**–**7**, **9** and **11** is probably explained as follows: these two-electron oxidation processes are regarded as an electrochemical–electrochemical–chemical process, in which the chemical step probably involves great structural rearrangement (see below). If the rate of the latter step is slow the oxidation wave would be accompanied by a reduction wave similar to the oxidation wave (as for **5** and **7**), but if the rate is fast the new reduction wave would appear at a different potential (as for **6**, **9** and **11**). Surprisingly, the oxidation potential of **6**, **7** and **11** is remarkably lower ($\Delta E = 0.52$, 0.43 and 0.32–0.34 V, respectively) than that of pentamethylruthenocene ($E_{pa} = +0.33$ V). Similarly, complexes **5** and **9** showed lower oxidation potentials by 0.52 and 0.37–0.33 V than that of ruthenocene ($E_{pa} = +0.55$ V). Another example of a compound containing two ruthenocene parts which shows such an unusual low oxidation potential was [1.1]ruthenocenophane,[11a] which is oxidized to the dicationic complex containing a direct Ru^{III}–Ru^{III} bond.[11c] The two-electron process observed in **5**–**7**, **9** and **11** is considered to be due to two one-electron oxidation processes (of $Ru^{II/III}$) for each ruthenocene moiety, suggesting that there is a certain ligand-mediated metal–metal interaction between the two ruthenium atoms. This unique behavior in 1,2-bis(ruthenocenyl)ethylenes may be interpreted as follows. The crucial interaction takes place potentially between the two filled non-bonding d orbitals of the ruthenocene part and the filled



Scheme 3 (i) *p*-Benzoquinone (2 equivalents)–BF_3·OEt_2 (10 equivalents), CH_2Cl_2, 0 °C; (ii) *p*-benzoquinone (2 equivalents)–BF_3·OEt_2 (10 equivalents), CH_2Cl_2, −78 °C

bonding orbital of the ethylene part, leading to a splitting of these orbitals into three new filled orbitals, *i.e.* bonding, non-bonding and antibonding. This is similar to the result obtained from Fenske–Hall MO calculations on butadienediyl-bridged diiron complexes.[21] The interaction does not contribute to the metal–metal interaction in the neutral complex because of no net stabilizing energy. However, on oxidation, an electron is removed from the new highest filled orbital and this reflects the lowering of the oxidation potential, as observed in complexes **5**–**7**, **9** and **11**. The extent of the shift to lower potential of the first oxidation wave would be modified by the methyl-substitution mode on the C_5H_5 ring or the bridging ethylene. The electron-donating effect of the methyl group decreases the oxidation potential. Also, the effect of the methyl substituent on the inclination of the plane of the C_5H_4 from the plane of the ethylene bond seems to reduce the extent of the low-potential shift and to influence the stability of the two-electron oxidized species (see below).

Complexes **5**–**7** were oxidized with 2 equivalents of benzoquinone–BF_3·OEt_2 at 0 °C in CH_2Cl_2 to give the corresponding dicationic complexes **12**–**14** as stable solids in moderate to good yields (Scheme 3). Dimethyl analogs **9a** and **9b** similarly gave the oxidized species **15a** and **15b** at −78 °C in CH_2Cl_2, respectively, but no stable oxidation product from **11a** and **11b** could be isolated. The oxidized complexes were soluble in CD_3CN, but not in acetone and CH_2Cl_2. The complexes **12**–**14** were stable in CD_3CN at room temperature for a long time, but solutions of **15a** and **15b** in CD_3CN decomposed at room temperature within 1 h. The instability of the latter may be because of the increased strain induced by the methyl group on the *exo*-methylene carbon. The IR spectrum of **13** showed very strong absorption of ν_{BF} at 1084 cm^{-1}, indicating that **13** is a cationic complex having BF_4^- as counter anion. The cyclopentadienyl protons in the oxidized complex **13** shifted downfield ($\Delta \approx 1.4$ ppm), implying the accumulation of positive charge on the Ru atom. In spite of this, a high-field shift of the olefinic proton from δ 5.92 in the neutral complex **6** to δ 5.60 in **13** was observed, suggesting co-ordination of the olefinic carbon. One of the most interesting points observed for the oxidized species is the chemical shift (δ 96.76 for **13**) and the $^1J_{CH}$ coupling constant (167 Hz for **13**) of the carbon atoms connecting the two ruthenocenyl moieties. These values are very similar to those of the *exo*-methylene carbon in the tetramethylfulvene complex [Ru(η^5-C_5H_5)(η^6-$C_5Me_4CH_2$)]BF_4 (δ 69.40 and $^1J_{CH}$ = 167 Hz)[17] and [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]PF_6 (δ 77.77 and $^1J_{CH}$ = 165 Hz),[22a,b] rather than those of the olefinic carbon (δ 121.69 and $^1J_{CH}$ = 153 Hz in **6**). Similar ^{13}C spectral features were also observed for complexes **12** (δ 91.34 $^1J_{CH}$ = 170 Hz) and **14** (δ 87.05, $^1J_{CH}$ = 165 Hz). The protons of the substituted C_5H_4 in ^1H NMR spectrum of **13** were observed as two double triplets and two triple doublets, although the latter is somewhat broadened. Such asymmetric appearance is in accord with no rotation around the *exo* double bond. Based on the proton coupling pattern of the cyclopentadienyl rings in ferrocene derivatives,[23,24] the double triplets at δ 4.93 and 5.43 observed for complex **13** can be assigned as the α-C_5H_4 protons, and the triple doublets at δ 5.86 and 5.98 as the β-C_5H_4 protons. This assignment was confirmed by two-dimensional H–H COSY measurement; the latter signals gave a correlation peak but the former no such peak. The appearance of the α-C_5H_4 protons at higher field than that of the β-C_5H_4 protons is characteristic of fulvene complexes.[25] A similar asymmetric pattern of the C_5H_4 ring protons and a similar H–H COSY spectrum were observed for complex **12**, as well as for **15a** and **15b**. These spectral data suggest that **12**–**15** can be assigned as (μ-η^6:η^6-pentafulvadiene)diruthenium complexes. The separation ($\Delta \approx 15$ ppm) of the α- and β-protons of the substituted C_5H_4 ring in **13** is rather larger than that ($\Delta \approx 9$ ppm) of **12**, as well as that ($\Delta \approx 11$ ppm) of **15a** and **15b**, suggesting that the fulvenic structure may contribute more to the limiting structure in the former than in the latter complexes.

A single crystal X-ray analysis of complex **13** was performed[15] and selected bond distances and angles are summarized in Table 3. The C_5Me_5 ligand is normal (C–C average 1.43 Å). The distance of the C_5H_4 ring from the Ru atom is 1.811 Å and somewhat shorter than the distance between the C_5Me_5 ring and the Ru atom (1.825 Å). The tilt angle between the C_5Me_5 and C_5H_4 rings is 11.29° and significantly different from the corresponding value (32.2°) of [Ru(η^5-C_5H_5)$_2$I]I_3[26] and similar to that (6.9°) of the isomorphous osmium analog[22c] of the cationic fulvene complex [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]-BPh_4,[22d] respectively. This suggests that the oxidation state of the central atom of complex **13** remains Ru^{II}. Some bond alternation is observed in the substituted C_5H_4 ligand of **13**, although it is somewhat obscure because of the disorder described above than that in the cationic fulvene complex [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]BPh_4.[22d] The C(1A/1B)–C(2) distance (average 1.48 Å) is shorter than the corresponding distance in the neutral complex **6** (average 1.55 Å). The Ru–C(2) distance [2.077(5) Å] is somewhat shorter than Ru–C(3) [2.159(6) Å] and Ru–C(6) [2.174(6) Å]. Moreover, the Ru–C(1A/1B) distance (average 2.41 Å) and the bending angle of the C(2)–C(1A/1B) bond from the plane of the substituted C_5H_4 ring to the Ru atom (40.4°) are close to the corresponding values in [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]BPh_4 [2.270(3) Å and 40.3°][22d] and the isoelectronic [Cr(η^6-$C_5H_4CH_2$)(CO)$_3$] [2.352(9) Å and 35°],[25a] respectively. The distance (average 1.46 Å) of the central bond connecting the halves of the molecule **13** is close to that of a sp^2–sp^2 single bond (1.47 Å). These features indicate that the halves of the molecule have the structure of a fulvene complex and therefore the total molecule of **13** is assigned as a (μ-η^6:η^6-pentafulva-

Table 3 Selected bond distances (Å) and angles (°) for complexes **13** and **15b**

13		**15b**	
Ru(1)–C(1A)	2.407(1)	Ru(1)–C(1)	2.571(4)
Ru(1)–C(1B)	2.413(1)	Ru(1)–C(5)	2.116(4)
Ru(1)–C(2)	2.077(5)	Ru(1)–C(6)	2.180(4)
Ru(1)–C(3)	2.174(6)	Ru(1)–C(7)	2.224(5)
Ru(1)–C(4)	2.244(7)	Ru(1)–C(8)	2.217(4)
Ru(1)–C(5)	2.225(7)	Ru(1)–C(9)	2.162(4)
Ru(1)–C(6)	2.159(6)	Ru(2)–C(2)	2.474(4)
		Ru(2)–C(15)	2.090(4)
		Ru(2)–C(16)	2.175(4)
		Ru(2)–C(17)	2.212(5)
		Ru(2)–C(18)	2.216(4)
		Ru(2)–C(19)	2.167(4)
C(1A)–C(1A)	1.467	C(1)–C(2)	1.491(5)
C(1B)–C(1B)	1.444	C(1)–C(3)	1.512(6)
		C(2)–C(4)	1.514(6)
C(1A)–C(2)	1.453(6)	C(1)–C(5)	1.406(5)
C(1B)–C(2)	1.519(6)	C(2)–C(15)	1.407(5)
C(2)–C(3)	1.445(10)	C(5)–C(6)	1.449(6)
C(2)–C(6)	1.418(10)	C(5)–C(9)	1.461(5)
C(3)–C(4)	1.376(11)	C(6)–C(7)	1.395(6)
C(4)–C(5)	1.414(13)	C(7)–C(8)	1.414(7)
C(5)–C(6)	1.373(12)	C(8)–C(9)	1.398(6)
		C(15)–C(16)	1.445(6)
		C(15)–C(19)	1.460(6)
		C(16)–C(17)	1.398(7)
		C(17)–C(18)	1.414(7)
		C(18)–C(19)	1.403(6)
Ru(1)–C($\mathrm{C_5Me_5}$)	2.195*	Ru(1)–C(ring)	2.184*
		Ru(2)–C(ring)	2.178*
C–C($\mathrm{C_5Me_5}$)	1.434*	C–C(ring)	1.396*
		C(2)–C(1)–C(3)	117.3(3)
		C(2)–C(1)–C(5)	121.1(3)
		C(3)–C(1)–C(5)	120.4(4)
		C(1)–C(2)–C(4)	116.4(4)
		C(1)–C(2)–C(15)	120.9(3)
		C(4)–C(2)–C(15)	121.0(4)

* Average.

diene)diruthenium complex. Free pentafulvadiene was reported as unstable and reactive red-violet crystals by Prinzbach and co-workers in 1977.[27] Complexes **12**–**14** are the first examples of transition-metal stabilized pentafulvadiene complexes, to the best of our knowledge. The pentafulvadiene ligand constitutes a plane with many folds, to which the two (η^5-$\mathrm{C_5Me_5}$)Ru parts are co-ordinated *anti* to each other. Moreover, the $\mathrm{C_5Me_5}$ rings in the two parts are also parallel to each other.

Single crystals of complex **15b** were fortunately obtained by recrystallization from $\mathrm{CH_3CN}$–diethyl ether at low temperature, in spite of the instability of the complex in solution. Selected bond distances and angles are summarized in Table 3. The ORTEP view of the cationic part of **15b** is given in Fig. 4. The structure is essentially similar to that of **13**. The remarkable features are the appearance of a cationic pentafulvadiene complex and the maintenance of the original *cis* conformation. The $\mathrm{C_5H_4}$ ring is practically flat and is located at somewhat shorter distance (1.810 and 1.799 Å) from the central Ru atom than that (1.825 and 1.825 Å) of the $\mathrm{C_5H_5}$ ring. The tilt angles between the $\mathrm{C_5H_5}$ and $\mathrm{C_5H_4}$ rings are 11.04(3) and 12.94(3)° similar to those in **13**. In the substituted $\mathrm{C_5H_4}$ ligand of **15b** there is a more clear bond alternation compared with that in **13**, as can been also seen in the cationic fulvene complex [Ru(η^5-$\mathrm{C_5Me_5}$)(η^6-$\mathrm{C_5Me_4CH_2}$)]$\mathrm{BPh_4}$[22d] and the fulvene complexes [Ru(η^6-$\mathrm{C_5Me_4CH_2}$)(η^4-$\mathrm{C_8H_{12}}$)],[28] [{$\mathrm{RuCl_2}$(η^6-$\mathrm{C_5Me_4CH_2}$)}$_2$],[29] [RuCl(η^2-Bu^{t}NSPh)(η^6-$\mathrm{C_5Me_4CH_2}$)][30] and [Cr(η^6-$\mathrm{C_5H_4CH_2}$)(CO)$_3$].[25a] The C(1)–C(5) and C(2)–C(15) distances [1.406(5) and 1.407(5) Å, respectively] are much shorter than the corresponding distances in the neutral complex **9b** [1.475(9) and 1.471(9) Å, respectively]. The C(5)–C(6) and C(5)–C(9) distances [1.449(6) and 1.461(5) Å, respectively] are long and C(6)–C(7) and C(8)–C(9) [1.395(6) and 1.398(6) Å] are short. A similar trend was observed in the C(15)–C(19) ring. The Ru(1)–C(5) distance [2.116(4) Å] is somewhat shorter than Ru(1)–C(6) and Ru(1)–C(9) [2.180(4) and 2.162(4) Å, respectively]. This trend can also be seen in the remaining half of the complex. Also, the Ru(1)–C(1) and Ru(2)–C(2) distances [2.571(4) and 2.474(4) Å, respectively] are somewhat longer than the corresponding values in **13** (average 2.41 Å), [Ru(η^5-$\mathrm{C_5Me_5}$)(η^6-$\mathrm{C_5Me_4CH_2}$)]$\mathrm{BPh_4}$ [2.270(3) Å],[22d] [{$\mathrm{RuCl_2}$(η^6-$\mathrm{C_5Me_4}$-$\mathrm{CH_2}$)}$_2$] [2.268(4) and 2.271(4) Å],[29] and the isoelectronic [Cr(η^6-$\mathrm{C_5H_4CH_2}$)(CO)$_3$] [2.352(9) Å].[25a] Moreover, the bending angles of the C(5)–C(1) and C(15)–C(2) bonds from the plane of the substituted $\mathrm{C_5H_4}$ ring to the Ru atom (29.1 and 29.1°, respectively) are smaller than in other related complexes (35–40°). These facts suggest that the bond between the Ru atom and the fulvene ligand in **15b** is somewhat weak because of the steric strain due to the methyl group on the bridging carbons. The distance [1.491(5) Å] of the central bond connecting the halves of the molecule **15b** is close to that (1.46 Å) in **13** and corresponds to a C–C single bond, implying that **15b** can also be assigned as a (μ-η^6:η^6-pentafulvadiene)diruthenium complex. The torsion angle C(3)–C(1)–C(2)–C(4) is 55.1(5)°, suggesting retention of the s-*cis* conformation which originates in the *cis* configuration in **11b**. The plane formed by C(2), C(1) and C(3) is inclined by 30.22° to that of the $\mathrm{C_5H_4}$ ring [C(5)–C(9)] and the plane formed by C(1), C(2) and C(4) is inclined by 33.70° to that of the $\mathrm{C_5H_4}$ ring [C(15)–C(19)] in **15b**. Such a strongly twisted structure seems to weaken the bond between the Ru atom and the fulvene ligand and make complex **15b** unstable.

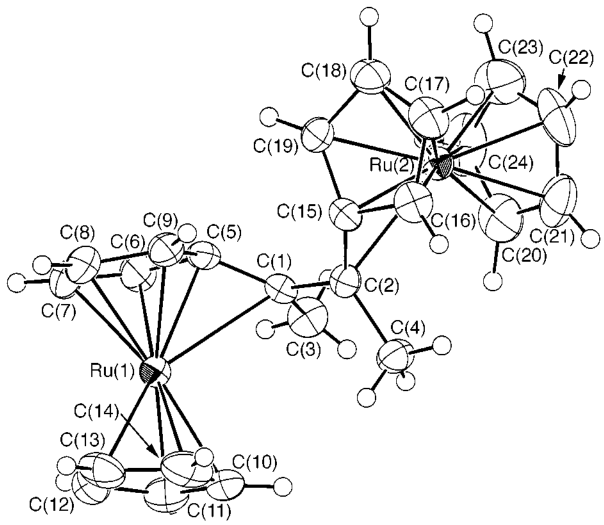
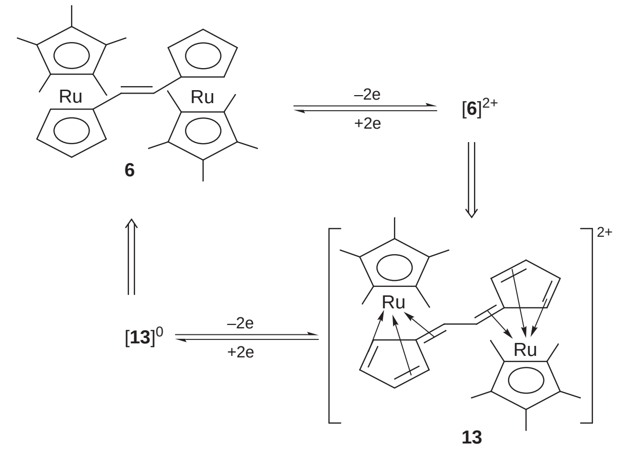


Fig. 4 An ORTEP view of the cationic part of complex **15b**

The formation of the (μ-η^6:η^6-pentafulvadiene)diruthenium complexes, **11**–**13**, **15a** and **15b**, in the two-electron oxidation of the corresponding ethylene derivatives may be explained as follows. As described above, the interaction between the filled bonding orbital of the ethylene part and the two filled non-bonding d orbitals of the ruthenocene parts would result in three new filled MOs. The removal of two electrons from the highest filled orbital (HOMO) leaves two pairs of electrons in non-bonding and bonding orbitals. As a result, a three-center four-electron (3c4e)-like interaction may be expected in the ethylene-bridging bis(ruthenocenyl) system and seems to bring about a large stabilization of the system and a structural rearrangement, *i.e.* the formation of the (μ-η^6:η^6-pentafulvadiene)diruthenium complexes. This interaction is very similar to that in the conversion of a butadienediyldiiron complex into a bis(carbene)-type complex upon two-electron oxidation.[31,32] A similar oxidative transformation accompanied by a structural rearrangement was also observed in sp carbon-bridged



Scheme 4 Square scheme for complex **6**

dirhenium complexes,[33] and fulvalene-[34] and cyclooctatetraene-bridged dinuclear complexes.[35]

In CH_2Cl_2–CH_3CN (6:4 v/v) solution,‡ the neutral ethylene **6** shows an irreversible two-electron oxidation wave at −0.18 V (for $Ru^{II}_2 \longrightarrow Ru^{III}_2$) and a smaller irreversible reduction wave ($E_{pc} = -0.32$ V) on the backward scan, and the dicationic complex **13** shows an irreversible two-electron reduction wave at −0.41 V (for $Ru^{II}_2 \longrightarrow Ru^{I}_2$) and a smaller irreversible oxidation wave ($E_{pa} = -0.17$ V) on the backward scan. These redox behaviors are very similar, although the redox potentials are slightly different. This suggests that the structural rearrangement induced by electron transfer in **6** and **13** may be chemically reversible. Actually, two-electron chemical reduction of the dicationic complex **13** by 2 equivalents of cobaltocene ($E^{\circ\prime} = -1.34$ V *vs.* ferrocene–ferrocenium in CH_3CN) gave the neutral complex **6** in 97% yield, although the reaction is very slow. Then, the redox reaction interrelating **6** with **13** may be explained by the process shown in Scheme 4, which is similar to a square scheme proposed by Geiger.[36] The reversibility of this redox system was confirmed by controlled potential electrolysis monitored by Raman spectra as shown in Fig. 5. The peak at 1641 cm^{-1} assigned to the C=C stretching vibration is weakened and that at 1530 cm^{-1} is increased according to the progress of oxidation. On reduction the reverse phenomena took place. The spectral changes were reproduced repeatedly. However, in the optically transparent thin layer electronic spectra (OTTLE) recorded upon controlled potential electrolysis a somewhat different behavior was observed as shown in Fig. 6. On oxidation of complex **6** the peaks at 340 and 440 nm increased and the absorption at 290 nm decreased, showing an isobestic point (at 316 nm), but the reductive scan of the oxidized solution showed the reverse change and no isobestic point. This seems to suggest that the oxidation proceeds rapidly and the intermediate ($[\mathbf{6}]^{2+}$) cannot be detected even if it exists, but that the reduction is slow and the intermediate ($[\mathbf{13}]^0$) may have a short lifetime. The latter observation is in accord with the slow chemical reduction of **13** by cobaltocene. The observation of good reversibility between **6** and **13** upon controlled potential electrolysis may be because Raman spectroscopy observes the stretching vibration of only the special bond in the molecule.

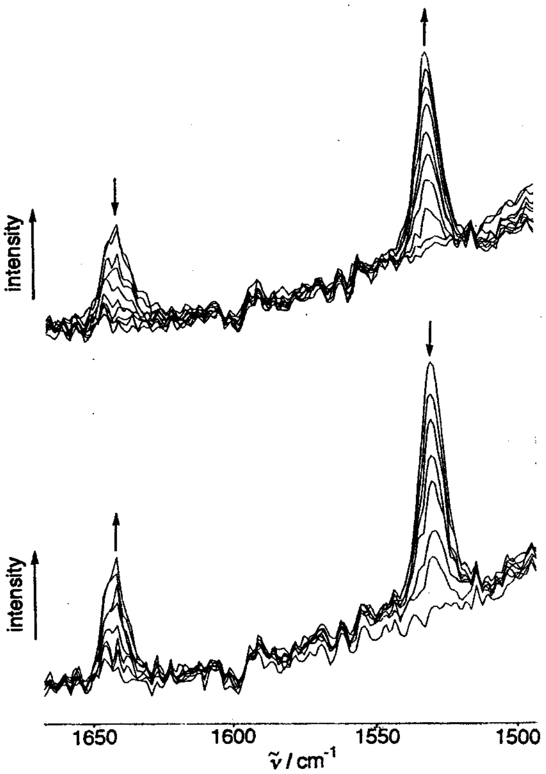


Fig. 5 Raman spectra (interval *ca.* 3 min) in the controlled potential electrolysis of complex **6** (1 mM) in CH_2Cl_2–CH_3CN (6:4, v/v). Upper: anodic electrolysis (potential limit 1.04 to +5.4 V). Lower: cathodic re-electrolysis (potential limit +0.54 to −1.04 V)

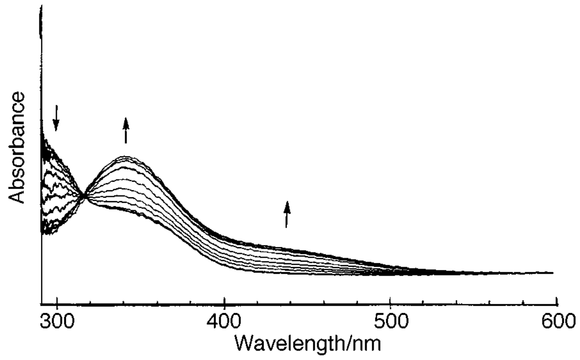


Fig. 6 Optical transparent thin layer electronic spectra (interval *ca.* 10 min) in the controlled anodic electrolysis (potential limit −0.40 to +0.50) of complex **6** in CH_2Cl_2–CH_3CN (6:4, v/v)

Experimental

All reactions were carried out under an atmosphere of N_2 and/or Ar and work-ups were performed without precautions to exclude air. The NMR spectra were recorded on Bruker AM400 or ARX400 spectrometers, IR and Raman (KBr disc) spectra on a Perkin-Elmer System 2000R spectrometer, electronic spectra on a Shimadz UV-2100 and Raman spectra upon controlled potential electrolysis on a Kaiser Optical Systems Holo Probe 532. Controlled potential electrolysis with a platinum mesh working electrode under an atmosphere of He and cyclic voltammetry were carried out by using BAS CV27 in 10^{-1} M $NBu^n_4ClO_4$ (polarography grade, Nacalai tesque) solution in CH_2Cl_2 and/or CH_3CN. The cells were fitted with a glassy carbon (GC) working electrode, platinum wire counter electrode and a Ag–Ag^+ pseudo-reference electrode, and the scan rate was 0.1 V s^{-1}. All potentials were referred to ferrocene–ferrocenium, the value for which was obtained by subsequent measurement under the same conditions.

Solvents were purified by distillation from the drying agent prior to use as follows: CH_2Cl_2 ($CaCl_2$), $ClCH_2CH_2Cl$ ($CaCl_2$), CH_3CN (CaH_2), thf (sodium–benzophenone) and diethyl ether ($LiAlH_4$). Formylruthenocene **4**,[18] 1,2,3,4,5-pentamethylruthenocene **1**[37] and $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_5Me_4CH_2)]BF_4$[17] were prepared according to the literature. Other reagents were used as received from commercial suppliers.

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‡ In order to compare directly redox behavior of **8** with that of **11**, the mixed solvent system was used for reasons of solubility.

Preparations

1-Formyl-1′,2′,3′,4′,5′-pentamethylruthenocene 2. A solution of Vilsmeier's complex was prepared by adding dmf (0.7 cm^3, 45 mmol) and subsequently $POCl_3$ (0.8 cm^3, 42 mmol) at 0 °C in 1,2-dichloroethane (15 cm^3) and stirring for 0.5 h at room temperature. To the yellow solution was added 1,2,3,4,5-pentamethylruthenocene **1** (1.28 g, 4.2 mmol). The solution was stirred for 12 h at 80 °C (oil-bath temperature) and then poured into aqueous saturated Na_2CO_3 solution (50 cm^3) and stirred for 0.5 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (50 cm^3 × 3). The organic layer and the extracts were collected, dried over $MgSO_4$, and then evaporated by a rotary evaporator. The residue was subjected to column chromatography on alumina using CH_2Cl_2 as the eluent. The yellow fraction was collected and evaporated to give complex **2** as a yellow solid. An analytically pure sample was obtained by sublimation [100 °C, 10^{-2} Torr, (*ca.* 1.33 Pa)] 1.20 g (87%). M.p. 82–84 °C (Found: C, 58.60; H, 6.13. $C_{16}H_{20}ORu$ requires C, 58.34; H, 6.12%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1676 (C=O). ^1H NMR ($CDCl_3$): δ 1.87 (s, 15 H, Me), 4.53 (t, *J* = 1.8, 2 H, β-H), 4.65 (t, *J* = 1.8 Hz, 2 H, α-H) and 9.40 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ 11.63 (Me), 72.57 (β-C of C_5H_4), 77.31 (α-C of C_5H_4), 84.71 (*ipso*-C of C_5H_4), 87.18 (C_5Me_5) and 189.39 (CHO).

1-Formyl-2,3,4,5-pentamethylruthenocene 3. *Path A.* Complex **1** (589 mg, 1.95 mmol) was refluxed with activated MnO_2 (Aldrich) (3.0 g) in 1,2-dichloroethane (60 cm^3) for 4 h. After MnO_2 had been filtered off the filtrate was evaporated by a rotary evaporator. The residue was subjected to column chromatography on alumina using CH_2Cl_2 as the eluent. From the first colorless fraction the starting material **1** was recovered in 40% yield (236 mg). The second yellow fraction was collected and evaporated in vacuum to give complex **3** as a yellow solid. An analytically pure sample was obtained by recrystallization from hexane, 226 mg (37%). M.p. 151–152 °C (Found: C, 57.22; H, 5.79. $C_{15}H_{18}ORu$ requires C, 57.13; H, 5.75%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1673 (C=O). ^1H NMR ($CDCl_3$): δ 2.01 (s, 6 H, β-Me), 2.18 (s, 6 H, α-Me), 4.35 (s, 5 H, C_5H_5) and 10.11 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ 11.64 (β-Me), 12.11 (α-Me), 73.49 (C_5H_5), 80.00 (β-C of C_5Me_4CHO), 87.26 (α-C of C_5Me_4CHO), 90.29 (*ipso*-C of C_5Me_4CHO) and 191.66 (CHO). The third yellow fraction gave 1,2-diformyl-3,4,5-trimethylruthenocene in 7% yield (45 mg) as yellow crystals. An analytically pure sample was obtained by recrystallization from hexane. M.p. 186–187 °C (Found: C, 54.81; H, 4.88. $C_{15}H_{16}O_2Ru$ requires C, 54.70; H, 4.90%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1678 (C=O). ^1H NMR ($CDCl_3$): δ 2.08 (s, 3 H, β-Me), 2.28 (s, 6 H, α-Me), 4.55 (s, 5 H, C_5H_5) and 10.30 (s, 2 H, CHO). ^{13}C NMR ($CDCl_3$): δ 11.13 (β-Me), 12.40 (α-Me), 74.92 (C_5H_5), 81.96 [β-C of $C_5Me_3(CHO)_2$], 92.33 [α-C of $C_5Me_3(CHO)_2$], 94.46 [*ipso*-C of $C_5Me_3(CHO)_2$] and 191.34 (CHO).

Path B. 1-Hydroxymethyl-2,3,4,5-pentamethylruthenocene (304 mg, 0.96 mmol) was refluxed with activated MnO_2 (7.5 g) in 1,2-dichloroethane (40 cm^3) for 4 h. After MnO_2 had been filtered off the filtrate was evaporated in vacuum. The residue was subjected to column chromatography on alumina using CH_2Cl_2 as the eluent. The first yellow fraction gave complex **3** as a yellow solid in 24% yield (73 mg). The second yellow fraction gave 1,2-diformyl-3,4,5-trimethylruthenocene in 21% yield (69 mg).

1-Hydroxymethyl-2,3,4,5-pentamethylruthenocene. To a solution of the fulvene complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_5Me_4CH_2)]BF_4$ (605 mg, 1.6 mmol) in thf (15 cm^3) was added 10% aqueous KOH solution (12 cm^3) at room temperature. The mixture was stirred for 10 min. After the solvent had been removed by a rotary evaporator the residue was extracted with CH_2Cl_2 (20 cm^3 × 3). The extracts were collected, washed with water (20 cm^3 × 3), dried over $MgSO_4$, and evaporated. The residue was recrystallized from hexane to give the analytically pure product as colorless crystals (464 mg, 96%). M.p. 109–110 °C (Found: C, 56.83; H, 6.32. $C_{15}H_{20}ORu$ requires C, 56.76; H, 6.35%). IR (KBr disc): 3460 cm^{-1} [ν(OH)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, *J* = 4.9, 1 H, OH), 1.94 (s, 6 H, β-Me of C_5Me_4), 1.96 (s, 6 H, α-Me of C_5Me_4), 3.97 (t, *J* = 4.9 Hz, 2 H, CH_2) and 4.33 (s, 5 H, C_5H_5). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.83 (β-C of C_5Me_4), 12.01 (α-C of C_5Me_4), 54.73 (CH_2), 72.04 (C_5H_5), 85.57 (β-CC_5Me_4), 86.31 (α-CC_5Me_4) and 94.49 (*ipso*-C of C_5Me_4).

***trans*-1,2-Bis(ruthenocenyl)ethylene 5.** To a low-valent titanium solution, prepared from $TiCl_4$ (0.6 cm^3, 5.3 mmol) in thf (30 cm^3) and zinc powder (700 mg, 10.9 mmol) at −78 °C, was added dropwise a solution of complex **4** (465 mg, 1.8 mmol) in thf (10 cm^3) at −78 °C. The brick-red reaction mixture was warmed to room temperature and then stirred for 12 h. To the resulting brown solution was slowly added water (15 cm^3). The mixture was stirred for 10 min and then acidified (to pH < 2) with hydrochloric acid. The resulting pale yellow powder was filtered off, washed with 10% aqueous HCl (10 cm^3 × 3) and CH_2Cl_2 (3 cm^3 × 3) and then dried in vacuum to give analytically pure **5**, 288 mg (66%). M.p. >230 °C (Found: C, 54.08; H, 4.10. $C_{11}H_{10}Ru$ requires C, 54.31; H, 4.14%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1645 (C=C). ^1H NMR ($CDCl_3$): δ 4.49 (s, 10 H, C_5H_5), 4.55 (t, *J* = 1.6, 4 H, β-2H of C_5H_4), 4.74 (t, *J* = 1.6 Hz, 4 H, α-H of C_5H_4) and 6.21 (s, 2 H, =CH). ^{13}C NMR ($CDCl_3$): δ 68.71 (β-C of C_5H_4), 70.35 (α-C of C_5H_4), 71.05 (C_5H_5) and 122.38 (=CH).

***trans*-1,2-Bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethylene 6.** To a low-valent titanium solution, prepared from $TiCl_4$ (0.15 cm^3, 0.17 mmol) in thf (12 cm^3) and zinc powder (174 mg, 2.7 mmol) at −78 °C, was added dropwise a solution of complex **2** (165 mg, 0.5 mmol) in thf (3 cm^3) at −78 °C. The brick-red reaction mixture was warmed to room temperature and then stirred for 4 h. To the resulting brown solution was added slowly a 10% aqueous K_2CO_3 solution (15 cm^3). The mixture was stirred for 10 min and then filtered. The filtrate was extracted with CH_2Cl_2 (20 cm^3 × 3). The extracts were collected, washed with water, dried over $MgSO_4$, and evaporated in vacuum. The residue was subjected to column chromatography on silica gel using a mixture of CH_2Cl_2 and hexane as the eluent. The first pale yellow fraction gave complex **6** as a yellow solid. An analytically pure sample was obtained by recrystallization from CH_2Cl_2–hexane, 146 mg (93%). M.p. 204–205 °C (Found: C, 60.84; H, 6.40. $C_{16}H_{20}Ru$ requires C, 61.32; H, 6.43%). Raman (KBr disc): $\tilde{\nu}$/cm^{-1} 1646 (C=C). IR KBr disc): $\tilde{\nu}$/cm^{-1} 1633 (C=C). ^1H NMR ($CDCl_3$): δ 1.86 (s, 30 H, Me), 4.19 (t, *J* = 1.4, 4 H, β-H of C_5H_4), 4.26 (t, *J* = 1.4 Hz, 4 H, α-H of C_5H_4) and 5.92 (s, 2 H, =CH). ^{13}C NMR ($CDCl_3$): δ 11.81 (Me), 70.78 (β-C of C_5H_4), 72.72 (α-C of C_5H_4), 85.12 (C_5Me_5), 87.36 (*ipso*-C of C_5H_4) and 121.69 (=CH).

***trans*-1,2-Bis(2,3,4,5-tetramethylruthenocenyl)ethylene 7.** Complex **7** was prepared from **3** (142 mg, 0.45 mmol) according to the procedure similar to that for **6**. Pale yellow crystals (102 mg, 76%). M.p. 221–222 °C (Found: C, 60.24; H, 6.07. $C_{15}H_{18}Ru$ requires C, 60.18; H, 6.06%). Raman (Kbr disc): $\tilde{\nu}$/cm^{-1} 1643 (C=C). ^1H NMR ($CDCl_3$): δ 1.99 (s, 12 H, β-Me), 2.07 (s, 12 H, α-Me), 4.20 (s, 10 H, C_5H_5) and 6.45 (s, 2 H, =CH). ^{13}C NMR ($CDCl_3$): δ 12.19 (β-Me), 13.16 (α-Me), 70.50 (C_5H_5), 84.08 (β-C of C_5Me_4), 86.28 (α-C of C_5Me_4), 87.15 (*ipso*-C of C_5Me_4) and 125.65 (=CH).

1,2-Dimethyl-1,2-bis(ruthenocenyl)ethylene 9a and 9b. To a solution of low-valent titanium, prepared by slow addition of titanium tetrachloride (0.2 cm^3, 1.8 mmol) to a suspension of zinc powder (0.23 g, 3.6 mmol) in thf (10 cm^3) at −78 °C, was added a solution of acetylruthenocene **8** (0.22 g, 0.8 mmol) at 0 °C. After stirring for 1 h on an ice-bath the mixture was gently refluxed for 2 h. An aqueous 10% potassium carbonate solution (10 cm^3) was added and the mixture stirred for 1 h at room temperature. The mixture was filtered and the residue washed with CH_2Cl_2. The filtrate and washings were combined and the organic layer was separated, washed with water, and then dried over $MgSO_4$. After evaporating under vacuum, the residue was subjected to column chromatography on SiO_2 by elution of hexane–toluene (2:1). Pale yellow crystals (0.17 g, 83%) were obtained. This compound was a mixture of *trans* and *cis* isomers, the ratio of which was determined from integration of the ^{1}H NMR spectrum to be *ca.* 2:3. The mixture was separated by a fractional recrystallization from chloroform–diethyl ether using the diffusion method. *trans*-**9a**: pale yellow, m.p. 210–211 °C (Found: C, 55.95; H, 4.67. $C_{12}H_{12}Ru$ requires C, 56.02; H, 4.67%); Raman (KBr disc) $\tilde{\nu}$/cm^{-1} 1622 (C=C); ^{1}H NMR ($CDCl_3$) δ 4.63 (t, J = 1.7, 4 H, α-H of C_5H_4), 4.55 (s, 10 H, C_5H_5), 4.54 (t, J = 1.7 Hz, 4 H, β-H of C_5H_4) and 1.97 (s, 6 H, Me); ^{13}C NMR ($CDCl_3$) δ 24.15 (Me), 69.26 (β-C of C_5H_4), 70.88 (C_5H_5), 71.59 (α-C of C_5H_4), 95.21 (*ipso*-C of C_5H_4) and 127.08 (C=). *cis*-**9b**: pale yellow, m.p. 203–205 °C (Found: C, 56.13; H, 4.68. $C_{24}H_{24}Ru_2$ requires C, 56.02; H, 4.67%); Raman (KBr disc) $\tilde{\nu}$/cm^{-1} 1623 (C=C); ^{1}H NMR ($CDCl_3$) δ 4.50 (s, 10 H, C_5H_5), 4.43 (t, J = 1.7, 4 H, α-H of C_5H_4), 4.40 (t, J = 1.7 Hz, 4 H, β-H of C_5H_4) and 1.84 (s, 6 H, Me); ^{13}C NMR ($CDCl_3$) δ 23.31 (Me), 69.02 (β-C of C_5H_4), 70.64 (C_5H_5), 72.02 (α-C of C_5H_4), 95.01 (*ipso*-C of C_5H_4) and 127.02 (C=).

1,2-Dimethyl-1,2-bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)-ethylenes 11a and 11b. These compounds were prepared from **10** according to the procedure described above. Pale yellow crystals (0.183 g, 70%) were obtained of a mixture of *trans* and *cis* isomers, the ratio of which was determined from integration of the ^{1}H NMR spectrum to be *ca.* 1:2. The mixture was separated by fractional recrystallization from benzene–diethyl ether using a diffusion method. *trans*-**11a**: pale yellow, m.p. 232–234 °C (Found: C, 62.78; H, 6.83. $C_{17}H_{22}Ru$ requires C, 62.36; H, 6.77%); Raman (KBr disc) $\tilde{\nu}$/cm^{-1} 1609 (C=C); ^{1}H NMR ($CDCl_3$) δ 4.35 (t, J = 1.7, 4 H, α-H of C_5H_4), 4.15 (t, J = 1.7 Hz, 4 H, β-H of C_5H_4), 1.98 (s, 6 H, =CMe) and 1.90 (s, 30 H, Me); ^{13}C NMR ($CDCl_3$) δ 11.88 (Me), 22.23 (=CMe), 72.49 (β-C of C_5H_4), 73.40 (α-C of C_5H_4), 84.81 (C_5Me_5), 94.37 (*ipso*-C of C_5H_4) and 125.67 (C=). *cis*-**11b**: pale yellow, m.p. 221–223 °C (Found: C, 62.71; H, 6.82. $C_{17}H_{22}Ru$ requires C, 62.36; H, 6.77%); Raman (KBr disc) $\tilde{\nu}$/cm^{-1} 1620 (C=C); ^{1}H NMR ($CDCl_3$) δ 4.06 (t, J = 1.6, 4 H, α-H of C_5H_4), 4.00 (t, J = 1.6 Hz, 4 H, β-H of C_5H_4), 1.86 (s, 6 H, =CMe) and 1.88 (s, 30 H, Me); ^{13}C NMR ($CDCl_3$) δ 11.92 (Me), 21.94 (=CMe), 71.86 (β-C of C_5H_4), 73.64 (α-C of C_5H_4), 84.72 (C_5Me_5), 95.30 (*ipso*-C of C_5H_4) and 125.53 (C=).

[Ru$_2$(μ-η^6:η^6-$C_5H_4CHCHC_5H_4$)(η^5-C_5H_5)$_2$][BF$_4$]$_2$ 12. To a solution of complex **5** (48.6 mg, 0.1 mmol) and *p*-benzoquinone (21.6 mg, 0.2 mmol) in CH_2Cl_2 (35 cm^3) was added BF_3·OEt_2 (0.13 cm^3, 1.0 mmol) at room temperature. The solution was sonicated for 30 min. The resulting orange powder was filtered off and washed with ether (2 cm^3 × 3). An analytically pure sample was obtained by recrystallization repeatedly from CH_3CN–diethyl ether, 66 mg (99%). M.p. >230 °C (Found: C, 40.15; H, 2.97. $C_{11}H_{10}BF_4Ru$ requires C, 40.03; H, 3.05%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1084 (BF_4). ^{1}H NMR (CD_3CN): δ 5.22 (m, 2 H, α-H of C_5H_4), 5.40 (s, 10 H, C_5H_5), 5.96 (broad d, J = 3.0, 2 H, α-H of C_5H_4), 6.19 (td, J = 3.0 and 0.9 Hz, 2 H, β-H of C_5H_4), 6.25 (s, 2 H, =CH) and 6.38 (broad t, 2 H, β-H of C_5H_4). ^{13}C NMR (CD_3CN): δ 84.88 (α-C of C_5H_4), 85.52 (α-C of C_5H_4), 87.86 (C_5H_5), 91.34 ($^1J_{CH}$ = 170 Hz, =CH), 94.02 (β-C of C_5H_4), 94.36 (β-C of C_5H_4) and 104.63 (*ipso*-C of C_5H_4).

[Ru$_2$(μ-η^6:η^6-$C_5H_4CHCHC_5H_4$)(η^5-C_5Me_5)$_2$][BF$_4$]$_2$ 13. To a solution of complex **6** (12.5 mg, 0.02 mmol) and *p*-benzoquinone (4.3 mg, 0.04 mmol) in CH_2Cl_2 (5 cm^3) was added BF_3·OEt_2 (0.02 cm^3, 0.2 mmol) at 0 °C. The solution was stirred for 10 min. The resulting red powder was filtered off and washed with ether (2 cm^3 × 3). An analytically pure sample was obtained by recrystallization from CH_3CN–ether, 9.3 mg (58%). M.p. >230 °C (Found: C, 48.04; H, 5.11. $C_{16}H_{20}BF_4Ru$ requires C, 48.02; H, 5.04%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1084 (BF_4). ^{1}H NMR (CD_3CN): δ 1.90 (s, 30 H, Me), 4.93 (m, 2 H, α-H of C_5H_4), 5.43 (broad d, 2 H, α-H of C_5H_4), 5.60 (s, 2 H, =CH), 5.86 (td, J = 2.9 and 0.9 Hz, 2 H, C_5H_4) and 5.98 (broad t, 2 H, C_5H_4). ^{13}C NMR (CD_3CN): δ 10.62 (Me), 81.59 (α-C of C_5H_4), 84.10 (α-C of C_5H_4), 96.76 (=CH, $^1J_{CH}$ = 167 Hz), 97.32 (β-C of C_5H_4), 99.15 (β-C of C_5H_4), 100.87 (C_5Me_5) and 106.37 (*ipso*-C of C_5H_4).

[Ru$_2$(μ-η^6:η^6-$C_5Me_4CHCHC_5Me_4$)(η^5-C_5H_5)$_2$][BF$_4$]$_2$ 14. Complex **14** was prepared from **7** according to a procedure similar to that for **13**. Orange crystals (9.4 mg, 61%). M.p. >230 °C (Found: C, 47.10; H, 4.54. $C_{15}H_{18}BF_4Ru$ requires C, 46.65; H, 4.70%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1084 (BF_4). ^{1}H NMR (CD_3CN): δ 1.79 (s, 6 H, Me), 2.12 (s, 6 H, Me), 2.23 (s, 6 H, Me), 2.29 (s, 6 H, Me), 5.19 (s, 10 H, C_5H_5) and 6.40 (s, 2 H, =CH). ^{13}C NMR (CD_3CN): δ 10.13 (Me), 11.71 (Me), 11.90 (Me), 13.52 (Me), 87.05 ($^1J_{CH}$ = 165 Hz, =CR), 99.70 (C_5Me_5), 100.14 (*ipso*-C of C_5Me_4), 100.55 (C_5Me_5), 109.34 (C_5Me_5) and 110.66 (C_5Me_5).

s-*cis*-[Ru$_2$(μ-η^6:η^6-$C_5Me_4CMeCMeC_5Me_4$)(η^5-C_5H_5)$_2$][BF$_4$]$_2$ 15b. *cis* Isomer **9b** (30.8 mg, 0.06 mmol) and *p*-benzoquinone (13 mg, 0.12 mmol) were dissolved in CH_2Cl_2 (10 cm^3) under N_2 and the solution was cooled to 0 °C; BF_3·OEt_2 (0.2 cm^3, 1.6 mmol) was added. After stirring for 1.5 h at 0 °C the red-brown oily product precipitated. The supernatant solution was removed by a syringe and MeCN (1 cm^3) and subsequently acetone (1 cm^3) was added. After addition of anhydrous ether (1 cm^3), the solution was chilled at −78 °C for 1 h. The resulting red-brown micro crystals were filtered off, 30 mg, (72%). M.p. 205 °C (decomp.) (Found: C, 41.85; H, 3.44. $C_{12}H_{12}BF_4Ru$ requires C, 41.89; H, 3.51%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1420, 1395, 1120–1000 and 859. ^{1}H NMR (CD_3CN): δ 6.41 (td, 2 H, J = 3.0 and 1.0, β-H of C_5H_4), 6.12 (td, 2 H, J = 3.0 and 1.0, β-H of C_5H_4), 5.50 (s, 5 H, C_5H_5), 5.46 (dt, 2 H, J = 3.0 and 1.0, α-H of C_5H_4), 5.15 (dt, 2 H, J = 3.0 and 1.0 Hz, α-H of C_5H_4) and 1.93 (s, 3 H, Me). ^{13}C NMR (CD_3CN): δ 28.05 (Me), 81.74 (β-C of C_5H_4), 83.04 (β-C of C_5H_4), 86.06 (C_5H_5), 92.89 (α-C of C_5H_4), 94.15 (*ipso*-C of C_5H_4) and 125.90 (=CMe).

s-*trans*-[Ru$_2$(μ-η^6:η^6-$C_5Me_4CMeCMeC_5Me_4$)(η^5-C_5H_5)$_2$]-[BF$_4$]$_2$ 15a. *trans* Isomer **9a** was oxidized according as described above giving red-brown micro crystals (32 mg, 77%) of **15a**, m.p. 195 °C (decomp.) (Found: C, 42.04; H, 3.44. $C_{12}H_{12}BF_4Ru$ requires C, 41.89; H, 3.51%). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1423, 1120–1000 and 850. ^{1}H NMR (CD_3CN): δ 6.38 (td, 2 H, J = 3.0 and 1.0, β-H of C_5H_4), 6.09 (td, 2 H, J = 3.0 and 1.0, β-H of C_5H_4), 5.48 (s, 5 H, C_5H_5), 5.42 (dt, 2 H, J = 3.0 and 1.0, α-H of C_5H_4), 5.14 (dt, 2 H, J = 3.0 and 1.0 Hz, α-H of C_5H_4) and 2.35 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 28.02 (Me), 81.73 (β-C of C_5H_4), 83.04 (β-C of C_5H_4), 86.04 (C_5H_5), 92.85 (α-C of C_5H_4), 94.13 (α-C of C_5H_4) and 104.09 (*ipso*-C of C_5H_4).

Two-electron reduction of complex 11 with cobaltocene. To a solution of complex **11** (32 mg, 0.04 mmol) in CH_3CN (9 cm^3) and CH_2Cl_2 (5 cm^3) was added cobaltocene (20 mg, 0.11 mmol) at room temperature. The solution was stirred for 12 h. The solvent was removed by a rotary evaporator and the residue subjected to column chromatography on silica gel using CH_2Cl_2–hexane (1:1 v/v) as the eluent. The pale yellow first fraction was collected and evaporated to give pure **6** (24 mg,

Table 4 Crystal and intensity collection data for complexes **6**, **9a**, **9b**, **13** and **15b**

	6	**9a**	**9b**	**13**	**15b**
Formula	$C_{22}H_{40}Ru_2$	$C_{24}H_{24}Ru_2$	$C_{24}H_{24}Ru_2$	$C_{32}H_{40}B_2F_8Ru_2$	$C_{24}H_{24}B_2F_8Ru_2$
M	626.80	514.59	514.59	800.42	688.21
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/a$	$P2_1/n$
a/Å	7.820(1)	5.9060(6)	11.5630(9)	13.905(3)	11.5740(6)
b/Å	8.573(3)	9.9670(9)	9.8190(6)	15.026(3)	9.5430(6)
c/Å	10.803(3)	16.049(1)	16.501(1)	7.900(3)	21.2030(8)
α/°	93.83(2)				
β/°	91.76(2)	93.640(6)	93.184(3)	91.76(2)	92.055(3)
γ/°	102.00(2)				
U/Å^3	706.1(3)	942.8(2)	1609.6(5)	1609.6(5)	2340.4(2)
Z	1*	2	4	2*	4
D_c/g cm^{-3}	1.47	1.812	1.817	1.65	1.953
Crystal dimensions/mm	0.30 × 0.18 × 0.16	0.5 × 0.15 × 0.15	0.35 × 0.14 × 0.14	0.20 × 0.17 × 0.12	0.12 × 0.12 × 0.1
μ/cm^{-1}	10.662	15.768	15.895	9.618	13.409
hkl Limits	−10 to 0, −10 to 11, −14 to 14	0–8, 0–14, −22 to 22	0–16, 0–13, −23 to 23	0–18, 0–19, −10 to 10	0–16, 0–13, −24 to 20
Total reflections measured	3581	3828	5680	4208	6273
Unique reflections	3239	2335	4275	3683	5080
Reflections used	2511	2335	4275	3094	5080
Parameters	241	166	331	284	421
R	0.021	0.038	0.041	0.040	0.032
R′	0.028	0.041	0.052	0.045	0.033
Maximum, minimum peaks in final Fourier map/e Å^{-3}	2.14, −0.73	0.75, −0.90	0.88, −0.77	1.08, −0.73	0.66, −0.75

* Crystal molecular symmetry 1.

97%) as a yellow solid. The spectroscopic data of the sample were identical with those of an authentic sample.

Crystallography

The crystallographic data are listed in Table 4. Data collections for complexes **6** and **13** were performed at room temperature on a Mac Science MXC18K diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) and an 18 kW rotating anode generator. The structure was solved with the DIRDIF-PATTY or SIR method in CRYSTAN-GM[38] and refined by full-matrix least squares. Absorption correction with the ψ-scan method and anisotropic refinement for non-hydrogen atom were carried out. Data collections for **9a**, **9b**, and **15b** were performed by the Weissenberg method on a Mac Science DIP3000 image processor under similar conditions for those above. The structure was solved with the SIR method in CRYSTAN-GM and refined by full-matrix least squares. An absorption correction by the DIFABS method[39] and anisotropic refinement for non-hydrogen atom were carried out. All the hydrogen atoms, located from Fourier difference maps, were isotopically refined.

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