(Pentamethylcyclopentadienyl)ruthenium Complexes. 6.[1] (Pentamethylcyclopentadienyl)(polyarene)ruthenium Cations. Synthesis and Electrochemical Reduction

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By treatment of the alkoxo complex [Cp*Ru(OMe)]₂ with acid or trimethylsilyl trifluoromethanesulfonate in the presence of a polycyclic arene, the monocations Cp*Ru(arene)⁺ (arene = naphthalene ([1]⁺), phenanthrene ([2]⁺), pyrene ([3]⁺), anthracene ([4]⁺)) and dications (Cp*Ru)₂(arene)²⁺ (arene = phenanthrene ([5]²⁺), pyrene ([6]²⁺), and anthracene ([7]²⁺)) were synthesized. Electrochemistry (cyclic voltammetry) in dichloromethane or propylene carbonate shows all these complexes, in contrast to the case for (Cp or Cp*)Ru(arene) (Cp = η⁵-C₅H₅, Cp* = η⁵-C₅Me₅) cations featuring an unfused aromatic ligand, to be reducible. Some of the electron couples are chemically reversible. Potentials and peak current ratios are discussed in terms of interaction of the Cp*Ru units and of stabilization of the reduction products.
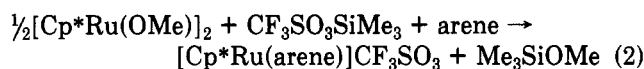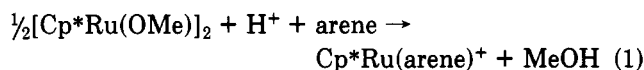
Introduction

Sandwich cations (Cp or Cp*)Fe(arene)⁺ (Cp = C₅H₅, Cp* = C₅Me₅) have shown an interesting and synthetically useful substitution and redox chemistry[2,3] and have in some cases offered the possibility for unusual transformations at the arene ligand.[4] In contrast, despite the fact that many Ru analogues have been prepared,[5] their chemistry appears to have been much less explored. The common procedure for the preparation of CpRu(arene) cations, which, as for the Fe congeners, consists of AlCl₃-catalyzed exchange of Cp or Cp* for an arene in ruthenocene or of substitution in (Cp or Cp*)Ru(CO)₂X,[6] in the case of polyaromatic ligands, has given only low yields.[7] A better route to these complexes was later found to be the reaction of [(Cp or Cp*)Ru(NCCH₃)₃]⁺ cations,[8] produced through photodecomplexation of (Cp or Cp*)-Ru(arene)⁺ salts in acetonitrile, with the respective polyaromatics,[9] to give derivatives of naphthalene, anthracene, pyrene, chrysene, and azulene in good yields. It was found that in these complexes the arene ligand is easily displaced by nucleophiles so that excess acetonitrile gives back the starting complex. More recently [Cp*RuCl]ₙ and Cp*Ru(acetone)⁺ were shown to be valuable precursors for the preparation of Cp*Ruᴵᴵ sandwich complexes with aromatic ligands of low π-acid potential such as pyridine, thiophene, and even furan.[10] None of these methods, however, have yielded complexes where more than one (Cp or Cp*)M moiety is bound to a fused aromatic system. The preparation and electrochemical investigation of such bis complexes, along with the corresponding mono complexes, are described for the first time below.

Results
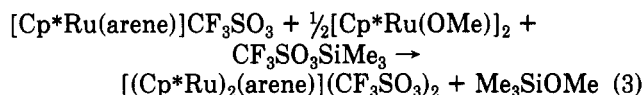
Preparations. The alkoxo complex [Cp*Ru(OMe)]₂[11]

has been found recently to be a convenient source of the cationic Cp*Ru⁺ fragment, which easily and quantitatively binds to arenes (eq 1); various noncomplexing acids such as HBF₄ and CF₃SO₃H can be used as proton sources.

$$\tfrac{1}{2}[Cp^*Ru(OMe)]_2 + H^+ + arene \rightarrow$$
$$Cp^*Ru(arene)^+ + MeOH \quad (1)$$

$$\tfrac{1}{2}[Cp^*Ru(OMe)]_2 + CF_3SO_3SiMe_3 + arene \rightarrow$$
$$[Cp^*Ru(arene)]CF_3SO_3 + Me_3SiOMe \quad (2)$$

Alternatively a methoxo group can be removed by the action of CF₃SO₃SiMe₃ (eq 2). We have utilized reactions 1 and 2 to generate Cp*Ru(arene)⁺ complexes [1]CF₃S-O₃–[4]CF₃SO₃. Complexes 1, 3, and 4 were previously reported.[9]
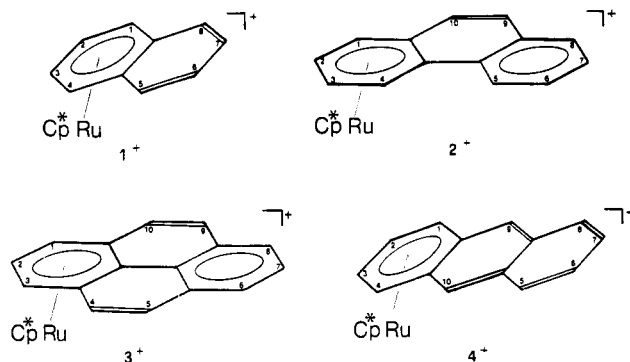
The Cp*Ru⁺ fragments obtained by the above reactions are active enough to allow complexation of two Cp*Ru units to one polyarene by treatment of the monocation with a second equivalent of [Cp*Ru(OMe)]₂ and acid (eq 3) in dichloromethane.[12]

$$[Cp^*Ru(arene)]CF_3SO_3 + \tfrac{1}{2}[Cp^*Ru(OMe)]_2 +$$
$$CF_3SO_3SiMe_3 \rightarrow$$
$$[(Cp^*Ru)_2(arene)](CF_3SO_3)_2 + Me_3SiOMe \quad (3)$$

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(12) There is a claim in the literature for the preparation of the bis-(cyclopentadienyl)iron dications of anthracene, phenanthrene, pyrene, and chrysene: Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603. Subsequent work[13] has confirmed that bis complexes do not form under the conditions employed and that the polyaromatics are hydrogenated. In particular, for the bis(anthracene) complex, where proton NMR data are given, the singlet for the 9- and 10-protons is attributed to a signal at about δ 5.5. These protons have been found to absorb at δ 9.09 in 7 (Table I). Moreover, the reduction potential given for the anthracene dication (Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500) is identical with the value quoted for the 9,10-dihydroanthracene dication.

Table I. ^{1}H NMR Absorptions (ppm) of Cationic Complexes [2]$^+$, [3]$^+$, and [5]$^{2+}$–[7]$^{2+}$

| compd no. (solvent)	
[2]$^+$ (acetone-d_6)	8.0 (H$_1$), 7.50 (H$_2$, H$_3$), 8.66 (H$_4$), 7.83 (H$_5$), 6.33 (H$_6$, H$_7$), 6.76 (H$_8$), 8.145, 7.759 (H$_9$, H$_{10}$), 1.59 (Cp*) $J_{9,10}$ = 9.31 Hz
[3]$^+$ (acetone-d_6)	6.46 d (H$_1$, H$_3$), 6.23 t (H$_2$), 7.53 d (H$_4$, H$_{10}$), 8.13 d (H$_5$, H$_9$), 8.1 m (H$_6$, H$_7$, H$_8$), 1.30 (Cp*) $J_{1,2}$ = $J_{2,3}$ = 5.1 Hz, $J_{4,5}$ = $J_{9,10}$ = 9.3 Hz
[5]$^{2+}$ (acetone-d_6)	6.82 (H$_1$, H$_8$), 7.45 (H$_4$, H$_5$), 6.47 (H$_2$, H$_7$), 6.52 (H$_6$, H$_3$), 7.75 (H$_9$, H$_{10}$), 1.73 (Cp*)
[6]$^{2+}$ (MeOH-d_4)	6.72 d (H$_1$, H$_3$, H$_6$, H$_8$), 6.46 t (H$_2$, H$_7$), 7.85 s (H$_4$, H$_5$, H$_9$, H$_{10}$), 1.53 (Cp*)
[7]$^{2+}$ (CD$_2$Cl$_2$)	7.28 (H$_2$, H$_3$, H$_6$, H$_7$), 6.14 (H$_1$, H$_4$, H$_5$, H$_8$), 9.09 (H$_9$, H$_{10}$), 1.61 (Cp*) $J_{1,2}$ = 4.5 Hz, $J_{1,3}$ = 2.5 Hz

Table II. Peak and Mean Potentials of Cationic Cp*Ru(arene) Complexes

compd no.	$-E_p^c(1)$, V	$-E_p^a(1)$	$-E_{1/2}(1)$,^{a}	v, mV/s
[1]$^+$	1.64	1.51	1.58	2000
[2]$^+$	1.91	1.70	1.80	20000
[3]$^+$	1.70	1.62	1.66	1000
[4]$^+$	1.35	1.21	1.28	20000

compd no.	$-E_p^c(1)$, V	$-E_p^a(1)$, V	$-E_{1/2}(1)$, V	$-E_p^c(2)$, V	$-E_p^a(2)$, V	$-E_{1/2}(2)$,^{b} V
[5]$^{2+\,c}$	1.45	1.35	1.40	1.66	1.51	1.58
[6]$^{2+\,d}$	1.33	1.26	1.295	1.57	1.49	1.53
[7]$^{2+}$	0.45^d	0.36^d	0.40^d	1.25^c	1.13^c	1.19^c

^{a} Peak and mean potentials of the single reduction. ^{b} Peak and mean potentials of the first and second reductions. ^{c} v = 5000 mV/s. ^{d} v = 100 mV/s.
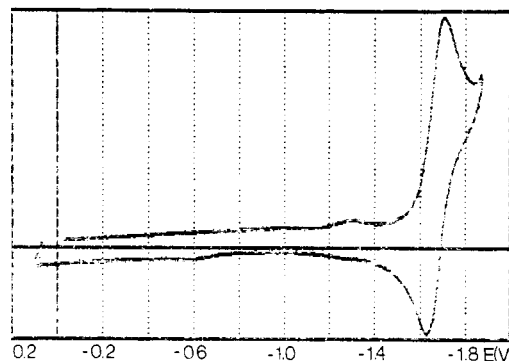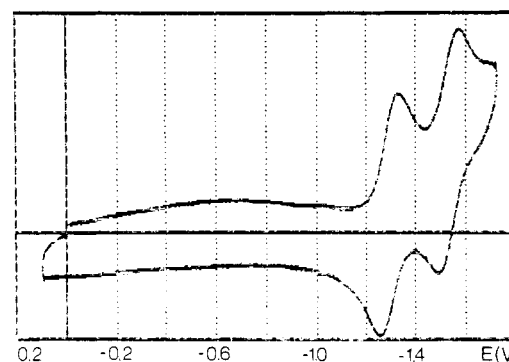
The yellow to green (anthracene) dications [5]–[7]$^{2+}$ are precipitated as PF$_6^-$ or CF$_3$SO$_3^-$ salts. Their structures
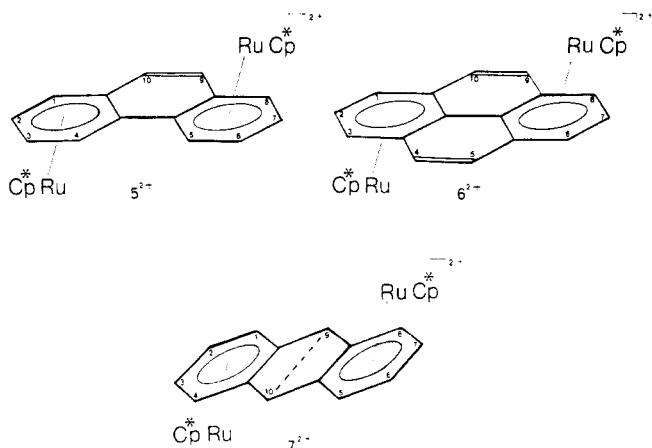
are deduced from ^{1}H NMR spectra, which, in contrast to the mono salts, show C_{2v} or C_s symmetry, giving rise to one set of protons at the complexed rings along with a singlet due to protons at the uncomplexed ring positions. NMR parameters, evaluated by computer simulation in the case of the more complex spectra of the monocations, are collected in Table I.

In no case was hydrogenation of the uncomplexed ring positions observed, in particular the 9,10-positions of anthracene, which had thwarted preparation of the analogous CpFe mono- and dications.[13] Integration of the ^{1}H NMR absorptions gives the expected intensity ratios.

Electrochemical Reduction. Whereas (Cp or Cp*)-Fe(arene)$^+$ cations are susceptible to chemical and electrochemical reduction to the neutral 19-electron sandwich complexes,[3] those of ruthenium have been found to resist reduction within the potential window of common solvents used in electrochemistry.[6] We find, by cyclic voltammetry,

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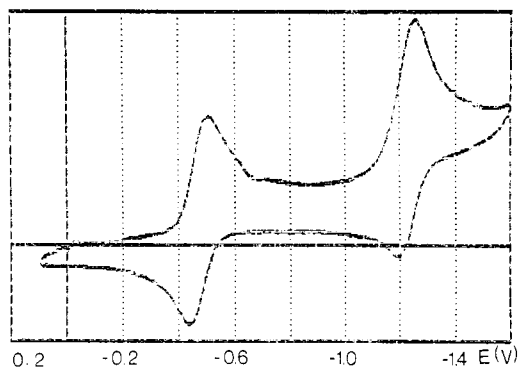**Figure 1.** Cyclic voltammogram of Cp*Ru(pyrene)$^+$ ([3]$^+$) in CH$_2$Cl$_2$ with v = 1000 mV/s.

Figure 2. Cyclic voltammogram of (Cp*Ru)$_2$(pyrene)$^{2+}$ ([6]$^{2+}$) in propylene carbonate with v = 1000 mV/s.

Table III. Peak Current Ratios i_c/i_a for the Reduction of Cations [1]$^+$–[7]$^+$ at Various Scan Rates

compd no.	i_a/i_c	v, mV/s	compd no.	i_a/i_c	v, mV/s
[1]$^+$	0	100	[3]$^+$	0.66	100
	0.8	2000		0.84	1000
[2]$^+$	0	5000	[4]$^+$	0	100
	0.61	20000		0.52	20000

compd no.	$i_a/i_c(1)$	$i_a/i_c(2)$	v, mV/s
[5]$^{2+}$	pr^a		5000
[6]$^{2+}$	1.04	pr	1000
[7]$^{2+}$	0.72	0	50
	0.72		100
	0.80	0.51	5000
	0.86	0.6	10000

^{a} Partly reversible.

ready electrochemical reduction of the mono as well as the bis Cp*Ru complexes in dichloromethane and propylene carbonate at the Pt or vitreous carbon electrode. Potentials are listed in Table II. The general pattern consists of one oxidation/reduction peak pair at –1.3 to –1.8 V vs SCE (–1.7 to –2.2 vs ferrocene/ferrocenium) of varying chemical reversibility for the monocations. An example is given in the cyclic voltammogram of [3]$^+$ in Figure 1. Peak current ratios at various scan rates are given in Table

Figure 3. Cyclic voltammogram of $(Cp^*Ru)_2(anthracene)^{2+}$ ($[7]^{2+}$) in CH_2Cl_2 with $v = 100$ mV/s.

III to illustrate the relative chemical stabilities of the reduction products.

The most negative reduction, that of the phenanthrene complex $[2]^+$, requires a scan rate of 20 V/s in order that the reoxidation peak of the neutral intermediate can be observed. The anthracene complex $[4]^+$ reduces also completely irreversibly at low scan rates, whereas the pyrene complex $[3]^+$ is partly reversible even at 100 mV/s and fully reversible at high scan rates.

The dications, as may be expected, are reduced electrochemically in two discrete steps; each step is assigned as a one-electron reduction. As can be seen from Figure 3, which shows the cyclic voltammogram of $[7]^{2+}$, the first reduction is at rather positive potential and is well separated from the second one, leaving a disproportionation potential of the monocation $[7]^+$ of -0.79 V. The radical $[7]^+$ could be genereated in situ by adding a stoichiometric amount of $CoCp_2$ ($E_{1/2} = -0.9$ V vs SCE in CH_2Cl_2) to the dichloromethane solution of $[7]^{2+}$. A dark blue-green color indicated the formation of the radical. The cyclic voltammogram of the anthracene complex was unchanged. As shown by a color change to yellow and the disappearance of the first reduction peak within about 15 min, the radical $[7]^+$ decomposes to $[4]^+$.

Discussion

The lower aromaticity in polyaromatics as compared to that in nonannelated arenes is responsible for the lower stability of the respective π-sandwich cations as exemplified by complexes bearing a Cp^*Ru residue. Lower aromaticity obviously facilitates electrochemical reduction to the extent that it is conveniently observed in the potential window provided by common organic solvents. Since reduction of monoarene cations has not been observed up to a potential of -2.5 V,[6] the displacement of the reduction potential as compared to that of monoarenes should thus be at least 1–1.3 V.

This contrasts with the case for CpFe(polyarene) cations, where the anodic displacement of the CpFe(naphthalene), -(pyrene), and -(phenanthrene) reduction potential vs that of the CpFe(benzene) cation is only 0.26, 0.16, and 0.12 V, respectively.[14] When Vlček's equation[14] ($d = (E^{\circ}_{C_1} - E^{\circ}_{C_2})/(E^{\circ}_{L_1} - E^{\circ}_{L_2})$), which allows an estimation of the relative ligand character d in the HOMOs of two related complexes C_1 and C_2 from the redox potentials of the complexes $E^{\circ}_{C_i}$ and the free ligands $E^{\circ}_{L_i}$, is applied, the potential separation observed for the Ru complexes leads to the conclusion that the ligand character of the HOMO is much greater; i.e., there is a more covalent metal–arene bond in the Ru as compared to that in the Fe complexes.

In no case is a distinct peak observed at more positive potentials after passage through an irreversible reduction peak. Such peaks, common for CpFe(arene) and many other 19-electron sandwich complexes,[15] would indicate oxidative cleavage of a dimer or oxidation of a hydrogenated $Cp^*Ru(\eta^5$-dienyl) neutral complex. Obviously short-lived neutral $Cp^*Ru(\eta^6$-arene) complexes undergo decomplexation rathere than dimerization or hydrogen abstraction. (Cyclic voltammograms are not altered in protic solvents, such as methanol.)

Two features are noteworthy in the cyclic voltammograms. One is the relative stability of the monocations derived from the bis complexes and the neutral complex derived from the mono complexes as indicated by peak current ratios for the first and second reductions collected in Table III. Inspection of Table III and of Figure 3 shows that electron transitions in the bis complexes generally are more reversible. Comparison of $[1]–[4]^+$ with $[5]–[7]^{2+}$ further reveals that monocations of the bis complexes are more stable than the neutral species derived from the mono complexes. In $[7]^{2+}$ the second reduction is clearly of lower chemical reversibility at a given scan rate (Figure 3); in $[5]^{2+}$ this seems to be reversed.

The second point to be noticed is the separation of the two reduction waves in bis complexes and the displacement of the first reduction toward more positive potential when mono and bis complexes are compared, which can be taken as a measure for the interaction of the two Cp^*Ru groups over the π system. Similar arguments have been presented in connection with electrochemical reduction of complexes featuring two $C_6Me_6Ru^+$ groups bound to a paracyclophane.[16] The smallest separation between the two consecutive reductions is 0.13 V found for $[5]^{2+}$, followed by 0.25 V for $[6]^{2+}$, whereas in the anthracene dicationic complex $[7]^{2+}$ peak pairs are separated by as much as 0.7 V (Figure 3). Displacement of the first reduction wave toward a more positive potential, which for $2/5$ and $3/6$ amounts to 0.40 and 0.36 V, respectively, is found for $4/7$ to be 0.88 V, in accordance with the much larger peak separation. Note that the second reduction of the bis complexes is positive of the reduction of the mono complexes in all three cases where both complexes are available.

In the bis complexes $[5]^{2+}$ and $[6]^{2+}$ the two Cp^*Ru-(η^6-arene) units thus seem to be electronically well isolated and reduction of each is not much influenced by the other. The greater stability of the neutral bis complex as compared to that of the neutral mono complex for a particular arene ligand can be accounted for by a redistribution of electrons in structure 6 (a similar formula can be drawn for 5). The activation energy for this rearrangement seems to be small since peak separations for the second reduction are not dramatically increased over those of the first reduction. In each case a diene-like or quinoid structure of the annelating ring(s) is left in the neutral bis complex,
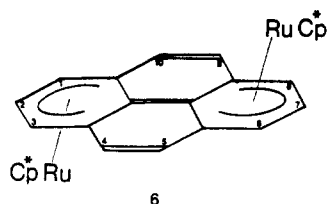
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which is energetically more favorable than the radical ensuing from reduction of the mono complexes, thus leading to a second reduction potential of the dications more positive than $E_{1/2}$ of the monocations.

The large interaction of the Cp*Ru units in the dication $[7]^{2+}$ must be intimately related to the structure of this complex. From Table II it is seen that the large potential separation of the two reduction steps is due to the easy reduction of the dication to the monocation being more positive in $[7]^{2+}$ than in $[5]^{2+}$ and $[6]^{2+}$ by about 1 V. This indicates extra free energy stored in the dication $[7]^{2+}$, which is released on the first reduction. The diamagnetism of the emerald green compound requires a coupling of the electrons remaining in positions 9 and 10 when two rings are η^6-bound to Cp*Ru.

Recent EHMO calculations[18] have shown the HOMO in 7^{2+} to be substantially composed of C9, C10 p_z orbitals ($\sim 70\%$). This means that coupling of the electrons formally confined to these positions is feasible without distortion of the planar geometry. The conspicuous green color of 7^{2+} as opposed to the yellow color of all other complexes may be related to the relatively small HOMO/LUMO separation in the anthracene dication.

Experimental Section

All preparations involving [Cp*Ru(OMe)]₂ have to be carried out under nitrogen. Since some dicationic complexes tend to be decomposed by donor solvents, workup was also done under nitrogen to avoid the interference of traces of water. Polyarenes were recrystallized commercial products. Cyclic voltammetry was performed with the previously described equipment.[17] The solvent was dichloromethane or propylene carbonate (Jackson, distilled); the supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH). Potentials are standardized to a ferrocene/ferrocenium potential of 0.4 V vs SCE.

Mono Complexes. (Pentamethylcyclopentadienyl)- (phenanthrene)ruthenium(II) Trifluoromethanesulfonate

([2]CF₃SO₃). Excess phenanthrene (150 mg, 0.84 mmol) was added to an ether solution of 140 mg (0.26 mmol) of [Cp*Ru-(OMe)]₂. When the mixture was homogeneous, 0.05 mL (0.55 mmol) of CF₃SO₃H was added with stirring. The color changed immediately from red to yellowish brown. After 1 h the precipitate was filtered, washed with several portions of ether to remove excess phenanthrene, and dried in vacuo. The crude product was dissolved in methylene chloride and absorbed onto a short column packed with Al₂O₃ (10% water). The column was washed with methylene chloride and the salt eluted with a 4:1 mixture of methylene chloride/acetone. After removal of the solvent there remained 96 mg (45%) of the product. Anal. Calcd for C₂₅-H₂₅F₃SO₃Ru (M_r 563.6): C, 53.28; H, 4.47. Found: C, 53.13; H, 4.38.

Mono complexes [1]CF₃SO₃, [3]CF₃SO₃, and [4]CF₃SO₃ were prepared similarly. For [1]⁺ HBF₄ was used and a BF₄⁻ salt isolated. [4]CF₃SO₃ was prepared according to eq 3, and treatment of the CF₃SO₃⁻ salt with NH₄PF₆ in 1:1 aqueous acetone precipitated the PF₆⁻ salt.

Bis Complexes. (Anthracene)bis((pentamethylcyclopentadienyl)ruthenium(II)) Bis(trifluoromethanesulfonate) ([7](CF₃SO₃)₂). To a solution of 54 mg (0.10 mmol) of [Cp*Ru(OMe)]₂ in 20 mL of dichloromethane was added 75 mg (0.13 mmol) of [4]CF₃SO₃. The reaction mixture was stirred for 5 min, and then 20 mL of 0.11 M CF₃SO₃SiMe₃ in dichloromethane was added dropwise with stirring. The solution changed from red to dark green within a few minutes. After 10 min the solvent was removed in vacuo and the residue washed with pentane and ether. It was purified two times by adding ether to a concentrated dichloromethane solution, which left 61 mg (48%) of green microcrystals. Anal. Calcd for C₃₆H₄₀F₆S₂O₆Ru₂ (M_r 948.9): C, 45.57; H, 4.25. Found: C, 45.30; H, 4.24.

By the same procedure the following compounds were obtained.

(Phenanthrene)bis((pentamethylcyclopentadienyl)ruthenium(II)) bis(trifluoromethanesulfonate) ([5](CF₃SO₃)₂): yield 45%. The product could not be freed from the accompanying Ru salt, which precluded satisfactory elemental analysis. Identification rests on the NMR data of Table I.

(Pyrene)bis((pentamethylcyclopentadienyl)ruthenium-(II)) bis(trifluoromethanesulfonate) ([6](CF₃SO₃)₂): yield 30%. Anal. Calcd for C₃₈H₄₀F₆S₂O₆Ru₂ (M_r 972.9): C, 46.91; H, 4.14. Found: C, 46.74; H, 4.13.