19-Electron arenecyclopentadienyl complexes of ruthenium

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A series of arenecyclopentadienyl complexes, *i.e.*, $[Ru(\eta^5\text{-}C_5R_5)(\eta^6\text{-arene})]^+$ (**1**, R = H, arene = C_6H_6; **2**, R = Me, arene = C_6H_6; **3**, R = H, arene = $C_6H_3Me_3$; **4**, R = Me, arene = $C_6H_3Me_3$; **5**, R = H, arene = C_6Me_6; **6**, R = Me, arene = C_6Me_6) was studied by cyclic voltammetry. These compounds are capable of both oxidation and reduction. The reduction potential values depend on the number of methyl groups in the complex. Reduction of benzene complexes **1** and **2** by sodium amalgam in THF leads to the formation of decomplexation products, the addition of hydrogen to benzene, and dimerization of the benzene ligands. Both chemical and electrochemical reductions of mesitylene complexes **3** and **4** result in dimeric products $[(\eta^5\text{-}C_5R_5)Ru(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Me_3H_3C_6C_6H_3Me_3)Ru(\eta^5\text{-}C_5R_5)]$ (**14**, R = H; **15**, R = Me). The action of sodium amalgam on compound **5** gives products of hydrogen addition to both hexamethylbenzene (**17**) and cyclopentadienyl (**18**) ligands along with the major product, the dimer $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Me_6C_6C_6Me_6)Ru(\eta^5\text{-}C_5H_5)]$ (**16**). In contrast to **5**, its permethylated analog **6** is only capable of adding hydrogen to the hexamethylbenzene ligand.

Key words: arenecyclopentadienyl complexes of ruthenium, synthesis, electrochemistry.

Previously,[1–4] we have studied methods for generating and reacting 19-electron sandwich complexes of platinum metals. In contrast to the relatively stable and well-studied 19-electron compounds of the first row transition metals,[5–8] the analogous complexes of transition metals of the second and third rows are highly reactive and readily enter into reactions involving both the formation and the cleavage of C—H and C—C bonds.[1–10] The steric and electron properties of cyclopentadienyl ligands significantly affect the reactivity of 19-electron metallocenes, as has been shown for rhodocene derivatives.[1,11,12] In the present work an attempt has been made to compare the influence of the nature of cyclopentadienyl and arene ligands on the reactivity of neutral arenecyclopentadienyl complexes of ruthenium.

In contrast to well-known 19-electron mixed sandwich complexes of iron $[Fe(\eta^5\text{-Cp})(\eta^6\text{-arene})]$,[5] the ruthenium analogs have virtually not been studied until the present time. It has been assumed that cationic monoarene complexes of ruthenium $[Ru(\eta^5\text{-Cp})(\eta^6\text{-arene})]^+$ are not reduced up to high negative potentials.[13,14] The reduction potential has been determined only for the compound $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$.[15] The preparative reduction of the latter by sodium amalgam resulted in a cyclohexadienyl complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)]$.[16] Later,[17] a number of mono- and binuclear complexes with fused aromatic ligands was studied by cyclic voltammetry (CV).

Results and Discussion

1. Studies of arenecyclopentadienyl complexes of ruthenium by CV

A series of arenecyclopentadienyl complexes of ruthenium **1**—**6** was studied by CV (see Table 1). The reduction of all compounds is one-electron and irreversible, which is evidence for high reactivity of the 19-electron intermediates formed. The cyclic voltammogram of compound **6** is shown in Fig. 1. The analogous curves for compounds **1**—**5** only differ in their quantitative characteristics. The reduction potentials of the complexes are shifted to more negative potentials as the number of methyl groups increases in both five- and six-membered rings. The increase in the potential due to each methyl group of the arene ligand is 31 mV. This value is close to that determined for a representative series of arene complexes (28 mV).[18] The value of the potential shift on going from cyclopentadienyl complexes to pentamethylcyclopentadienyl complexes varies in the range from 45 to 95 mV per methyl group for various compounds;[7,19] and amounts to 61 mV for compounds **1**—**6**.

We failed to observe the oxidation peak for the $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ complex (**1**) below +2.5 V, which is in agreement with the literature data.[13,14] The potentials of the peaks of irreversible oxidation for complexes **2**—**6** lie in a relatively narrow range from +1.9 V

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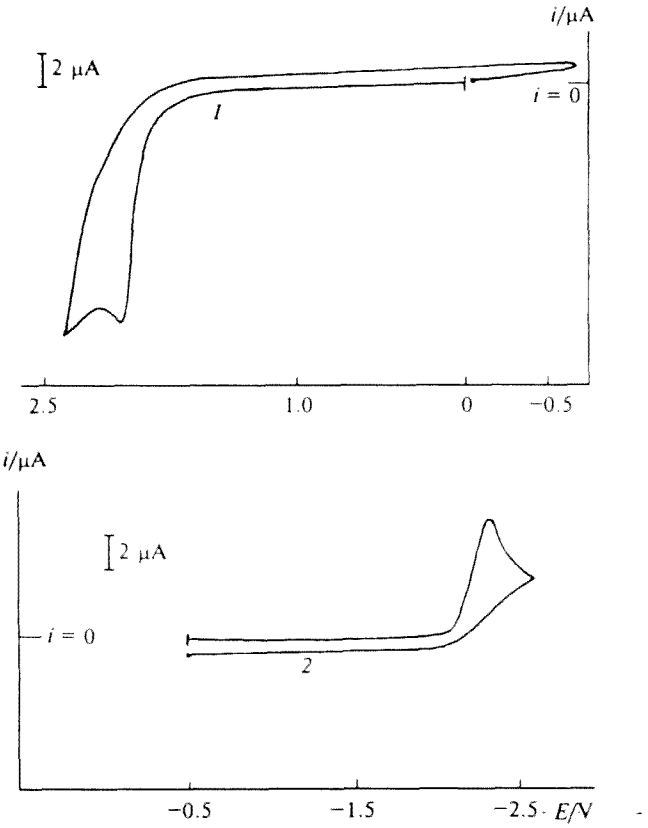


Fig. 1. Cyclic voltammogram of the complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$ ($C = 2 \cdot 10^{-3}$ mol L^{-1}, CH_3CN, 0.1 *M* Bu_4NBF_4, $V = 200$ mV s^{-1}, relative to SCE): *1*, oxidation; *2*, reduction.

to +2.2 V and depend weakly on the number of methyl substituents in the complex (Fig. 1, Table 1).

2. Reduction of arenecyclopentadienyl complexes of ruthenium

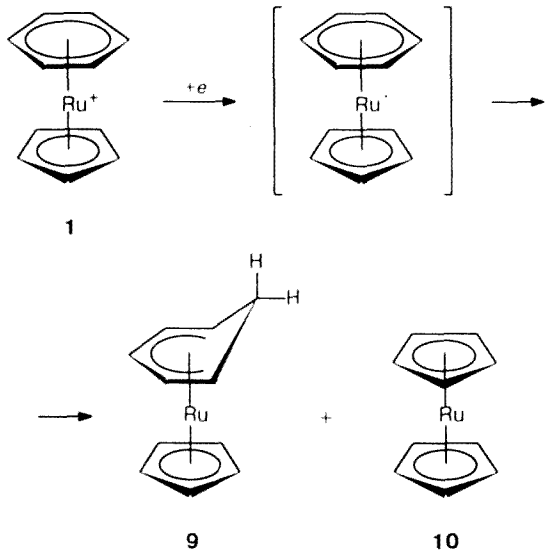
2.1. Reduction of $[Ru(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6H_6)]^+$ (1, R = H; 2, R = Me). Previously, in the reduction of complex **1** by 1 % sodium amalgam in THF (or in the two-phase pentane—water system), cyclohexadienyl complex **9** was isolated in low yield.[16] We attempted to reproduce the reduction of compound **1** by sodium amalgam in THF. Ruthenocene (**10**) was found to be the other product of this reaction along with cyclohexadienyl complex **9** (Scheme 1).

Table 1. CV data for complexes **1**—**6** ($C = 2 \cdot 10^{-3}$ mol L^{-1}, CH_3CN, 0.1 *M* Bu_4NBF_4, $V = 200$ mV s^{-1}, relative to SCE)

Complex	$E_{p,c}$ /V	$E_{p,a}$ /V
$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ (**1**)	−2.02	—
$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ (**2**)	−2.32	+2.11
$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**3**)	−2.13	+2.25
$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**4**)	−2.41	+2.12
$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ (**5**)	−2.18	+2.00
$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$ (**6**)	−2.51	+2.13

Note. $E_{p,a}$ and $E_{p,c}$ are potentials of anodic and cathodic peaks, respectively.

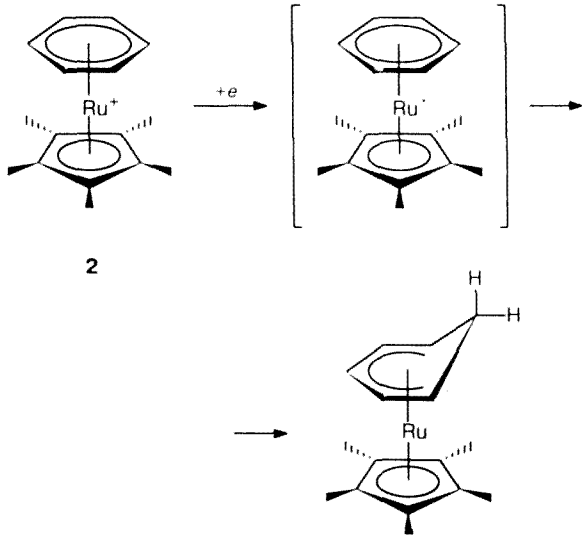
Scheme 1



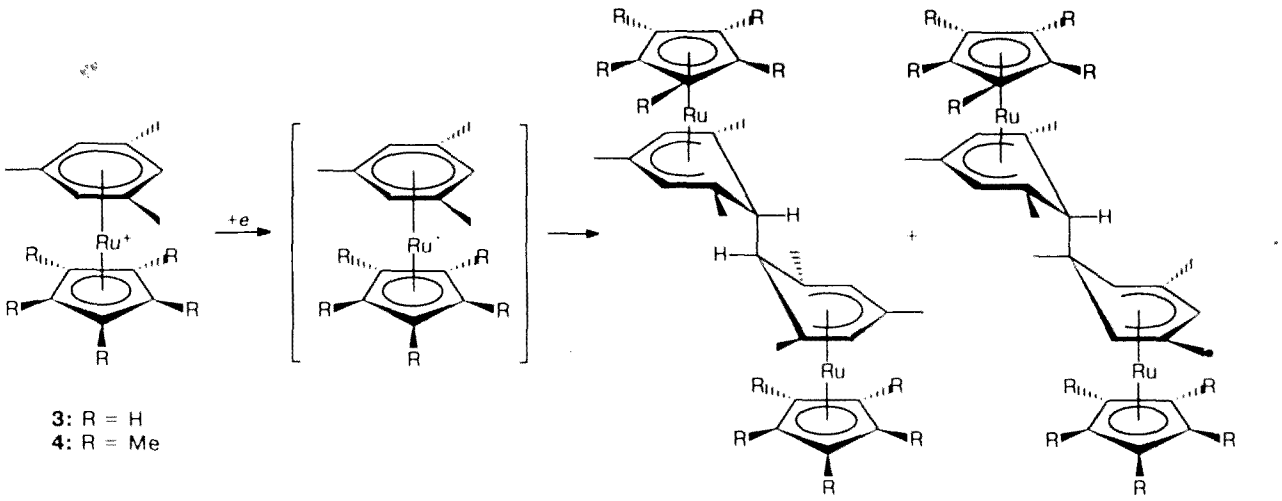
It is likely that the 19-electron radical formed in the reduction of **1** (as well as its iron analog[20,21]) is unstable and undergoes decomposition. The Cp^- anion, which is released in the process, enters a reaction with the $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^{\cdot}$ radical to give ruthenocene (**10**), similarly to the reduction of iron compounds.[22]

The product obtained in high yield in the reduction of pentamethylcyclopentadienyl complex **2** under the same conditions was cyclohexadienyl complex **11**. It is

Scheme 2



Scheme 3



likely that the presence of methyl substituents in the cyclopentadienyl ligand increases the stability of the 19-electron radical.

2.2. Reduction of $[Ru(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (3, R = H; 4, R = Me). Both the chemical reduction of **3** (1 % sodium amalgam, THF) and the electrochemical reduction of **4** (at a potential of −2.5 V, THF) result in the formation of the products of dimerization of the initially formed 19-electron radicals (Scheme 3). In each case, the dominant isomer is a dimer in which the mesitylene ligands are bonded through the unsubstituted carbon atoms (**14a**, **15a**). In addition to these, the asymmetric dimeric compounds **14b** and **15b** were found in mother liquors obtained when the reaction mixture was crystallized from hexane. According to ^{1}H NMR data, the yields of those isomers do not exceed 5—10 %. No formation of isomers in which the mesitylene ligands were bonded through two substituted carbon atoms was observed.

The dimerization of the mesitylene ligands in the reduction of the cationic complex $[Mn(\eta^6\text{-}C_6H_3Me_3)(CO)_3]^+$ proceeds with participation of either two substituted carbon atoms or one substituted and one unsubstituted carbon atom.[23] It is likely that because of the low electron-donor ability of the $Mn(CO)_3$ fragment, the inductive effect of the methyl groups leads to some increase in the electron density at the carbon atoms bonded to them, which makes those carbon atoms become favorable centers of dimerization. In our case, the strong electron-donor properties of the $Ru(\eta^5\text{-}C_5R_5)$ fragments level the spin electron density on the methylated and non-methylated carbon atoms of mesitylene, and the formation of isomers **14a** and **15a** is due to those insignificant steric hindrances that are exerted by the methyl groups of mesitylene.

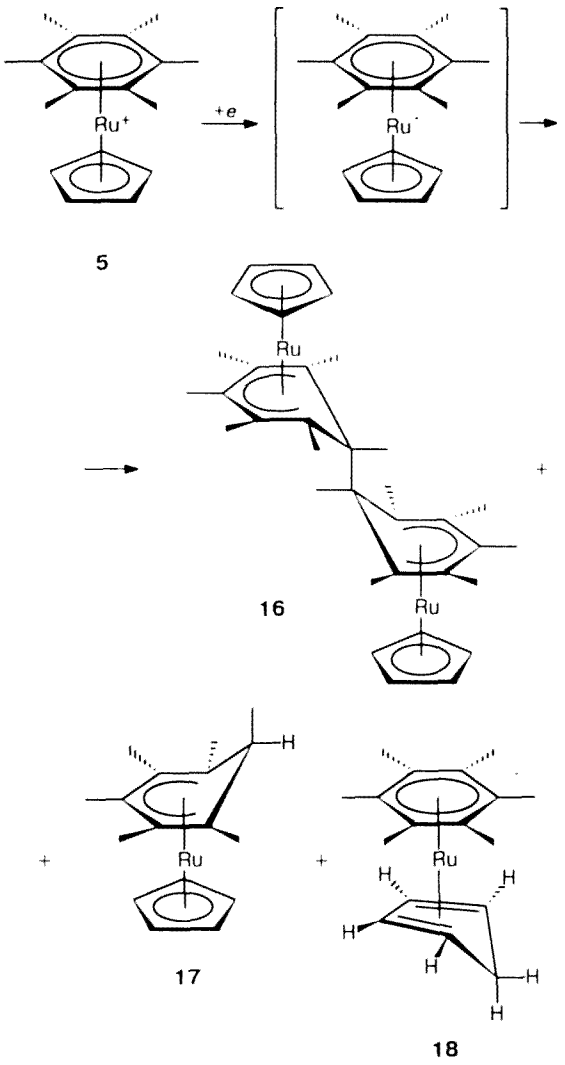
In contrast to benzene complexes **1** and **2**, the reduction of their mesitylene analogs **3** and **4** does not result in the formation of products of the addition of hydrogen to the mesitylene ligands. It is likely that this result can be explained by an increase in the stability of the 19-electron complexes as the number of methyl groups in the arene ligand increases.[18] As a consequence, two radicals manage to react with each other despite the presence of excess solvent, which is a donor of hydrogen atoms.

2.3. Reduction of $[Ru(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]^+$ (5, R = H; 6, R = Me). The reduction of hexamethylbenzene complex **5** by sodium amalgam in THF results in the formation of dimer **16** in 58 % yield (Scheme 4). It should be noted that the reduction of an analogous iron complex (unlike its less methylated complexes) gives a stable 19-electron radical not capable of dimerization.[20,21] Like in the case of ruthenium derivatives there is a greater tendency for the hapticity of complexes of transition metals of the second and third rows to change and for redistribution of the electron density.[7,18,21,24—27]

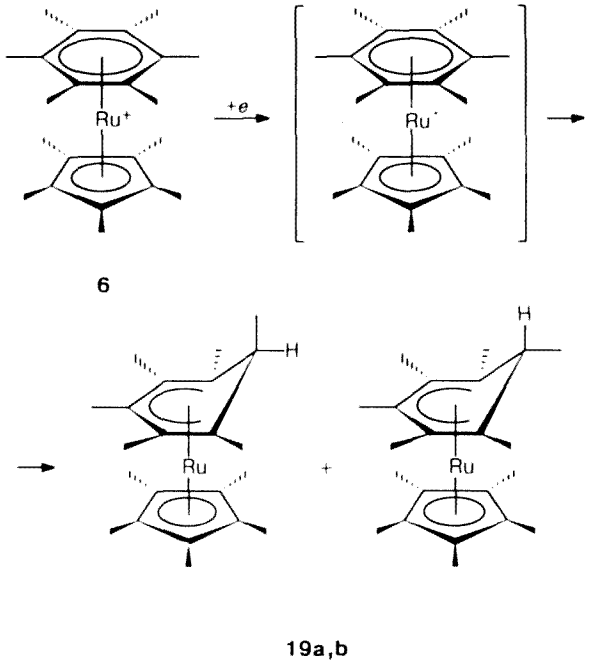
It was established using ^{1}H NMR spectroscopy that, besides complex **16**, two other compounds, the products of the addition of hydrogen to hexamethylbenzene (**17**) and cyclopentadienyl (**18**) ligands, are present in the reaction mixture. The content of compounds **17** and **18** is not high (~10 and 5 %, respectively).

Complex **6** was reduced electrochemically at a potential of −2.6 V (THF/0.2 *M* Bu_4NPF_6, Hg-electrode). A mixture of isomeric hexamethylcyclohexadienyl complexes **19a,b** (Scheme 5) was isolated from the electrolysis products. Unfortunately, one can not determine from the NMR spectra, which isomer (*exo*-H or *endo*-H) is the major one; the ratio of isomers is 1 : 6.

Scheme 4



Scheme 5



This difference in the behavior of hexamethyl complexes **5** and **6** could probably be explained by the excess electron density in permethylated compound **6**; it is so high that the process of the abstraction of hydrogen from the solvent proceeds faster than the dimerization of two radicals.

Thus, one-electron reduction of arenecyclopentadienyl cationic complexes of ruthenium results in the formation of highly-reactive neutral 19-electron radicals. Further reaction pathways of these compounds are determined by the presence and the number of methyl groups in the η^5- and η^6-bonded aromatic ligands. Thus, five-membered aromatic ligands, as a rule, do not participate in the reactions; however, the presence of methyl substituents in the C_5Me_5-rings increases the stability of the 19-electron complexes. An increase in the number of methyl substituents in the arene ligand also results in an increase in the stability of the radical compounds formed, and their dimerization becomes the preferred process. At the same time, in the case of permethylated complex **6** the total electron-releasing effect of eleven methyl groups is found to be so significant that only the addition of hydrogen to the hexamethylbenzene ligand is observed.

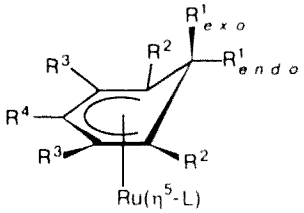
Experimental

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Tetrahydrofuran and benzene were distilled over benzophenone sodium ketyl before use; hexane was dried by boiling over a sodium wire; acetonitrile was purified by successive distillation over P_4O_{10}, $KMnO_4/NaHCO_3$, and CaH_2. Starting complexes of ruthenium were obtained using the known procedures: $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ (**1**);[13] $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ (**2**);[28] $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**3**);[29] $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**4**);[28] $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ (**5**);[29] $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$(**6**).[28]

CV data were obtained on a fast-acting potentiostat PI-50-1 in acetonitrile solutions at –20 °C under an argon atmosphere. Bu_4NPF_6 (0.1 *M*) was used as the supporting electrolyte, and a ferrocene/ferrocenium pair (E^0 = 0.40 V) was used as the internal standard. The concentrations of the substances under study and of the internal standard were $2 \cdot 10^{-3}$ mol L^{-1}. The potential scan rate was 200 mV s^{-1}. The measurements were carried out using a three-electrode scheme with a glassy-carbon electrode and a saturated calomel electrode (SCE) as the working electrode and the reference electrode, respectively. Potentials are given relative to SCE. The data obtained are presented in Table 1.

Potential-controlled electrolysis was performed using a P-5827M potentiostat in THF solutions under an argon atmosphere in an electrolyzer with cathodic and anodic spaces separated by a diaphragm of porous glass. A stirring Hg-cathode with an area of 11 cm^2 served as the working electrode and a platinum plate was used as the auxiliary electrode. Aqueous

Table 2. ^{1}H NMR spectra of the reduction products of complexes **1**—**6** (C_6D_6, δ, *J*/Hz, relative to $SiMe_4$)

Complex		R^1_{exo}, R^1_{endo}	R^2	R^3	R^4	L
	**9**	2.55—2.75 (m, 1 H); 2.85—3.00 (m, 1 H)	2.55—2.75 (m, 2 H)	4.45 (dd, 2 H, *J* = 6.0; *J* = 4.6)	5.76 (t, 1 H, *J* = 4.6)	4.72 (s, C_5H_5)
	11	1.60—1.95 (m, 2 H)	2.53 (m, 2 H)	4.08 (dd, 2 H, *J* = 5.9; *J* = 5.2)	5.20 (t, 1 H, *J* = 5.2)	1.87 (s, C_5Me_5)
	14a	1.98 (s, 2 H)	1.78 (s, 2 Me)	4.24 (s, 2 H)	2.31 (s, Me)	4.50 (s, C_5H_5)
	14b	1.29 (s, Me); 1.47 (s, 1 H)	1.81 (s, 2 Me); 2.37 (s, 2 H)	1.83 (s, 2 Me); 4.33 (s, 2 H)	2.27 (s, Me); 5.72 (s, 1 H)	4.52 (s, C_5H_5); 4.59 (s, C_5H_5)
	15a	1.86 (s, 1 H)	1.63 (s, 2 Me)	3.60 (s, 2 H)	2.10 (s, Me)	1.76 (s, C_5Me_5)
	16	1.31 (s, Me)	1.55 (s, 2 Me)	2.01 (s, 2 Me)	2.40 (s, Me)	4.32 (s, C_5H_5)
	17	0.46 (d, Me, *J* = 6.5); 2.46 (q, 1 H, *J* = 6.5)	1.80 (s, 2 Me)	1.98 (s, 2 Me)	2.39 (s, Me)	4.40 (s, C_5H_5)
	19a	0.55 (d, Me, *J* = 6.4); 2.22 (q, 1 H, *J* = 6.4)	1.53 (s, 2 Me)	1.95 (s, 2 Me)	2.10 (s, Me)	1.70 (s, C_5Me_5)
	19b	0.82 (d, Me, *J* = 6.5); 2.33 (q, 1 H, *J* = 6.5)	1.42 (s, 2 Me)	1.53 (s, 2 Me)	2.10 (s, Me)	1.72 (s, C_5Me_5)

SCE, connected to the solution in the electrolyzer with a salt bridge filled with the same solution as in the electrolyzer, served as the reference electrode. Before introduction of a substance under study, a solution of the supporting electrolyte was subjected to short-time electrolysis at the potential chosen for electrolysis of the complex under study on the basis of CV data. Electrolysis of complexes was performed until their disappearance (CV monitoring). The number of electrons participating in the electrode process was determined coulometrically using a Radelkis OH-404 (Hungary) digital coulometer.

^{1}H and ^{13}C NMR spectra were obtained on Bruker WP-200SY and Bruker-AMX-400 spectrometers in C_6D_6; chemical shifts are reported in the δ scale relative to $SiMe_4$. The data obtained are presented in Table 2 and Table 3.

Mass spectra were recorded on a Kratos MS-890 mass spectrometer.

Reduction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ (1), general procedure. A suspension of **1** (200 mg, 0.51 mmol) in THF (30 mL) was added to an excess of 1 % sodium amalgam and stirred for 2 h at ~20 °C. The reaction mixture was filtered and evaporated to dryness *in vacuo*. The solid residue was extracted with benzene (2×25 cm^3), the solution was filtered and evaporated. Recrystallization of the residue from hexane gave a mixture of **9** and **10** (69 mg, the ratio **9** : **10** = 2 : 1). MS (EI, 70 eV), *m/z*: 245 $[M]^+$ (**9**), 232 $[M]^+$ (**10**); ^{1}H NMR of **10** (C_6D_6), δ: 4.56 (s, 10 H).

Complexes **11**, **14**—**18** were reduced analogously.

Complex 11 (92 mg, 58 %) was obtained from **2** (200 mg, 0.50 mmol). Found (%): C, 62.05; H, 6.42. $C_{16}H_{22}Ru$. Calculated (%): C, 60.93; H, 7.03.

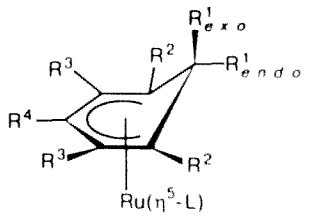
Complex 14. A mixture **14a,b** (85 mg, 65 %) was obtained from **3** (200 mg, 0.46 mmol). After recrystallization from hexane, yellow needle-shaped crystals were precipitated. The yield of **14a** was 62 mg (48 %). Found (%): C, 58.90; H, 6.10. $C_{28}H_{34}Ru_2$. Calculated (%): C, 58.72; H, 5.98. A mixture of **14a** and **14b** (23 mg, 17 %, the ratio **14a** : **14b** = 4 : 1) was obtained by evaporation of the mother liquor.

Complex 15 (106 mg, 74 %, the ratio **15a** : **15b** = 8 : 1) was obtained from **4** (200 mg, 0.40 mmol). Found (%): C, 65.28; H, 8.07. $C_{38}H_{54}Ru_2$. Calculated (%): C, 64.01; H, 7.63.

Complexes 16—18 were obtained from **5** (200 mg, 0.42 mmol). The yield of **16** was 81 mg (58 %). Found (%): C, 62.23; H, 7.29. $C_{34}H_{46}Ru_2$. Calculated (%): C, 62.17; H, 7.06. A mixture of **16**, **17**, and **18** (21 mg, the ratio **16** : **17** : **18** = 5 : 2 : 1) was obtained by evaporation of the mother liquor. ^{1}H NMR of **18** (C_6D_6), δ: 2.10 (s, 18 H, C_6Me_6); 2.31 (m, 2 H, H_α); 2.84 (ddd, 1 H, H_{endo}, *J* = 9.5, *J* = *J* = 1.6 Hz); 3.78 (d, 1 H, H_{exo}, *J* = 9.5 Hz); 4.69 (m, 2 H, H_β).

Electrochemical reduction of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+PF_6^-$ (4). Electrolysis of **4** (200 mg, 0.40 mmol) was carried out in THF (0.2 *N* Bu_4NPF_6) at a Hg-cathode at

Table 3. ^{13}C NMR spectra of the reduction products of complexes **1**—**6** (C_6D_6, δ, *J*/Hz, relative to $SiMe_4$)

Complex		CR^1_{exo}, R^1_{endo}	CR^2	CR^3	CR^4	L
	**9**	22.55 CH_2	30.18 CH	70.45 CH	78.82 CH	75.52 C_5H_5
	11	29.84 CH_2	32.87 CH	80.20 CH	88.51 CH	11.12 $C_5\underline{Me}_5$; 79.42 $\underline{C}_5Me_5$
	14a	58.95 CH	27.12 C<u>Me</u>; 40.91 <u>C</u>Me	79.25 CH	21.34 C<u>Me</u>; 90.47 <u>C</u>Me	77.71 C_5H_5
	15a	58.45 CH	24.17 C<u>Me</u>; 41.36 <u>C</u>Me	81.92 CH	19.24 C<u>Me</u>, 86.67 <u>C</u>Me	10.21 $C_5\underline{Me}_5$; 87.19 $\underline{C}_5Me_5$
	16	30.17 C<u>Me</u>; 52.38 <u>C</u>Me	18.95 C<u>Me</u>; 46.56 <u>C</u>Me	24.35 C<u>Me</u>; 89.59 <u>C</u>Me	18.03 C<u>Me</u>; 90.25 <u>C</u>Me	79.74 C_5H_5
	19a	13.80 C<u>Me</u>H; 49.62 <u>C</u>MeH	14.77 C<u>Me</u>; 39.20 <u>C</u>Me	19.74 C<u>Me</u>; 87.21 <u>C</u>Me	20.12 C<u>Me</u>; 90.46 <u>C</u>Me	9.42 $C_5\underline{Me}_5$; 85.97 $\underline{C}_5Me_5$

the potential $E = -2.5$ V. The starting current (25 mA) was smoothly reduced to 3 mA over a period of 45 min. The quantity of electricity consumed in the reduction process corresponded to the transfer of one electron (Q_{exp} = 39.1 C; $Q_{calc\ (n=1)}$ = 38.5 C). After electrolysis, a cyclic voltammogram showed the disappearance of the peak of reduction of the starting compound **4** and the appearance of one anodic oxidation peak ($E_{p.a.} = -0.27$ V). The electrolyzed solution was evaporated to dryness *in vacuo*, and the residue was extracted with benzene (2×25 cm^3). The combined benzene solution was filtered and evaporated, the residue was recrystallized from hexane, and a mixture of isomers **15a**/**15b** (97 mg, 68 %, the ratio **15a** : **15b** = 8 : 1) was obtained.

Electrochemical reduction of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ (6). Electrolysis of **6** (170 mg, 0.32 mmol) was carried out in THF (0.2 *N* Bu_4NPF_6) at a Hg-cathode at the potential $E = -2.6$ V. The starting current (20 mA) was smoothly reduced to 3 mA over a period of 40 min. The quantity of electricity consumed in the reduction process corresponded to the transfer of one electron (Q_{exp} = 32.1 C; Q_{calc} = 30.2 C). After electrolysis, a cyclic voltammogram showed the disappearance of the peak of reduction of the starting compound **6** and the appearance of the anodic peaks ($E_{p.a.}{}^1 = -0.08$ V and $E_{p.a.}{}^2 = +0.45$ V). The electrolyzed solution was evaporated to dryness *in vacuo*, the residue was extracted with benzene (2×25 cm^3). The combined benzene solution was filtered and evaporated, the residue was recrystallized from hexane, and a mixture of isomers **19a** and **19b** (75 mg, 60 %, the ratio **19a** : **19b** = 6 : 1) was obtained. Found (%): C, 66.37; H, 8.53. $C_{22}H_{34}Ru$. Calculated (%): C, 66.13; H, 8.58.

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