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Synthesis and reduction of trifluoromethyl-substituted arenecyclopentadienylruthenium sandwiches $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6R_6)]^+$ (R = H, Me) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+$ [1]

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Abstract

Dimer $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) has been prepared by reaction of $RuCl_3 \cdot (H_2O)_3$ with 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene in ethanol under reflux. Cationic arenecyclopentadienyl complexes $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-arene})]^+PF_6^-$ ($\mathbf{2}^+$, arene = C_6H_6; $\mathbf{3}^+$, arene = C_6Me_6) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+BF_4^-$ ($\mathbf{4}^+$) were obtained by refluxing $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) or $[Ru_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)_2]$ with corresponding arenes in alcohol. The redox properties of $\mathbf{2}^+$–$\mathbf{4}^+$ were studied by cyclic voltammetry (CV). All three complexes $\mathbf{2}^+$–$\mathbf{4}^+$ are reduced irreversibly in one-electron process. The values of reduction peak potentials for $\mathbf{2}^+$–$\mathbf{3}^+$ are less negative than those found for $\eta^5\text{-}C_5Me_5$ analogues. The reduction of $\mathbf{2}^+$ and $\mathbf{3}^+$ with sodium amalgam in tetrahydrofuran led to the formation of dimers $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_6H_6C_6H_6)]$ (**5**) and $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_6Me_6C_6Me_6)]$ (**6**) respectively. The reduction of $\mathbf{4}^+$ gave a non-identifiable mixture of neutral products. © 1998 Elsevier Science S.A.

Keywords: Ruthenium; Cyclopentadienyl; Arene; Cyclic voltammetry

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1. Introduction

The reduction of platinum metal sandwiches to 19-electron species was studied in our laboratory recently [1–7]. In contrast to the relatively stable and well-known first row transition metal 19-electron complexes [8–11], the analogous second and third transition row metal complexes are highly reactive [1–7,12–15]. It has been shown [5,7] that 19-electron arenecyclopentadienyl complexes of ruthenium bearing various number of methyl groups in arene or cyclopentadienyl ligands as well as complexes with polyaromatic ligands are more reactive than their iron analogues [8]. The 19-electron ruthenium complexes undergo either H-atom abstraction from solvent or dimerization [5,7]. The transformation process of these complexes is governed by steric and electronic properties of the ligands. The influence of electron-withdrawing substituents on the stability and reactivity of 19-electron complexes has not been studied so far.

The CF_3 group was selected for such a study because being unable to localize the unpaired electron density, conjugatively, it has a strong electron-withdrawing inductive influence. The 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene [16] was used for the preparation of CF_3-substituted ruthenium complexes. The ruthenium sandwich bearing CF_3 group in arene ligand

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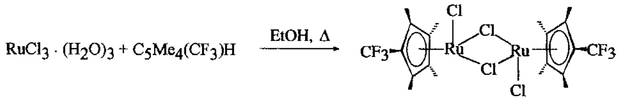
[1] With best wishes to Professor Peter Maitlis on his 65th birthday.



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Scheme 1.

was prepared from α,α,α-trifluorotoluene. We report here on the reduction of CF_3-substituted ruthenium sandwiches.

2. Results and discussion

2.1. Synthesis of trifluoromethyl-substituted ruthenium complexes

Ruthenocene $[Ru(\eta^5\text{-}(C_5Me_4CF_3)_2]$ has been prepared by long-time refluxing of $C_5Me_4CF_3H$ with $RuCl_3 \cdot (H_2O)_3$ in ethanol, as has previously been reported in Ref. [16]. We have found, however, that the dimer $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) can be obtained in 44% yield if the reaction is stopped after 2 h refluxing (Scheme 1).

The dimer **1** is a crystalline dark brown solid, unstable in solutions in air. It was characterized spectroscopically and by microanalysis (Table 1). Two broadened singlets arising from the Me groups were observed at δ -1.53 ($\Delta\nu = 25.6$ Hz) and 12.70 ($\Delta\nu = 36.7$ Hz) ppm in ^1H NMR spectrum. The CF_3 group shows singlet at δ 39.0 ($\Delta\nu = 65.0$ Hz) ppm in ^{19}F NMR spectrum. The chemical shifts and the form of signals confirm that **1** is paramagnetic [2] as it was earlier shown for pentamethylcyclopentadienyl analogue $[Ru_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)_2]$ [17–19].

The cationic sandwich complexes of ruthenium $\mathbf{2}^+$–$\mathbf{3}^+$ resulted from the reactions of dimer $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) in refluxing alcohol. To compare the influence of CF_3 group in cyclopentadienyl and arene ligands, sandwich complex $\mathbf{4}^+$ was prepared from $[Ru_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)_2]$ (Scheme 2).

Sandwiches $\mathbf{2}^+$–$\mathbf{4}^+$ were characterized by microanalysis and ^1H, ^{13}C and ^{19}F NMR spectroscopy (Tables 1–3).

2.2. Electrochemical study of complexes $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-arene})]^+$ ($\mathbf{2}^+$, arene $= C_6H_6$; $\mathbf{3}^+$, arene $= C_6Me_6$), and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+$($\mathbf{4}^+$)

Cationic sandwiches $\mathbf{2}^+$–$\mathbf{4}^+$ was studied by cyclic voltammetry (CV). The data obtained as well as the CV data for other arenecyclopentadienyl ruthenium complexes [5,7] are given in Table 4.

All three complexes $\mathbf{2}^+$–$\mathbf{4}^+$ are reduced irreversibly in one-electron process. The irreversibility of the reduction peaks indicates the high reactivity of 19-electron radicals formed. The supposition that these processes are one-electron is confirmed by the similarity of cathodic peak heights to those for ferrocenium used as an internal reference at the same concentration that is in agreement with the coulometry data (see below). The values of reduction potentials for $\mathbf{2}^+$ and $\mathbf{3}^+$ are less negative than for pentamethylcyclopentadienyl analogues (Table 4). The differences between the reduction potentials for $\mathbf{2}^+$ and $\mathbf{3}^+$ and the same values for analogous pentamethylcyclopentadienyl compounds are 0.35 and 0.39 V respectively. A suggestion has recently been made on the basis of photoelectron spectroscopy of transition metal complexes with $\eta^5\text{-}C_5Me_4CF_3$ ligand [16] that the latter is electronically similar to $\eta^5\text{-}C_5H_5$ ligand. This is in a good agreement with the fact that the values of reduction potentials for $\mathbf{2}^+$ and $\mathbf{3}^+$ and for cyclopentadienyl analogues are close.

The presence of trifluoromethyl group in $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+$ ($\mathbf{4}^+$) brings about the 0.36 V shift of the reduction potential to the region of less negative potential values in comparison with the potential value for $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Me)]^+$.

The oxidation of $\mathbf{2}^+$–$\mathbf{4}^+$ was not observed up to $+2.5$ V although other arenecyclopentadienyl ruthenium compounds were reported to undergo oxidation at these potentials [5,7]. Evidently, the presence of CF_3 substituents in $\mathbf{2}^+$–$\mathbf{4}^+$ results in the shifting of oxidation potential to the region of more positive potential values as it was shown for trifluoromethyl-substituted metallocenes of the iron group metals [20].

The bulk electrolyses of $\mathbf{2}^+$ and $\mathbf{4}^+$ were carried out at the first plateau potentials. Total amounts of 1.1 and 1.0 electrons were passed in the cases of $\mathbf{2}^+$ and $\mathbf{4}^+$ correspondingly. The reduction peaks of $\mathbf{2}^+$ and $\mathbf{4}^+$ disappeared after the electrolyses and new oxidation peaks were observed at $+0.26$ and $+0.19$ V. The re-oxidation of the resulting solutions led to the regeneration of $\mathbf{2}^+$ and $\mathbf{4}^+$.

Table 1
Yields and microanalysis data for complexes **1**–**6**

Complex	Yield, %	Microanalysis found (calculated)		
		C, %	H, %	F, %
1	44	33.50 (33.26)	3.35 (3.35)	15.16 (15.78)
$\mathbf{2}^+$	60	37.53 (37.44)	3.47 (3.53)	31.71 (33.31)
$\mathbf{3}^+$	51	43.98 (44.22)	4.98 (5.06)	28.39 (28.62)
$\mathbf{4}^+$	70	43.62 (43.52)	4.24 (4.30)	28.13 (28.34)
5	69	52.65 (52.17)	5.11 (4.93)	15.88 (15.47)
6	61	58.89 (58.39)	7.04 (6.68)	11.92 (12.59)

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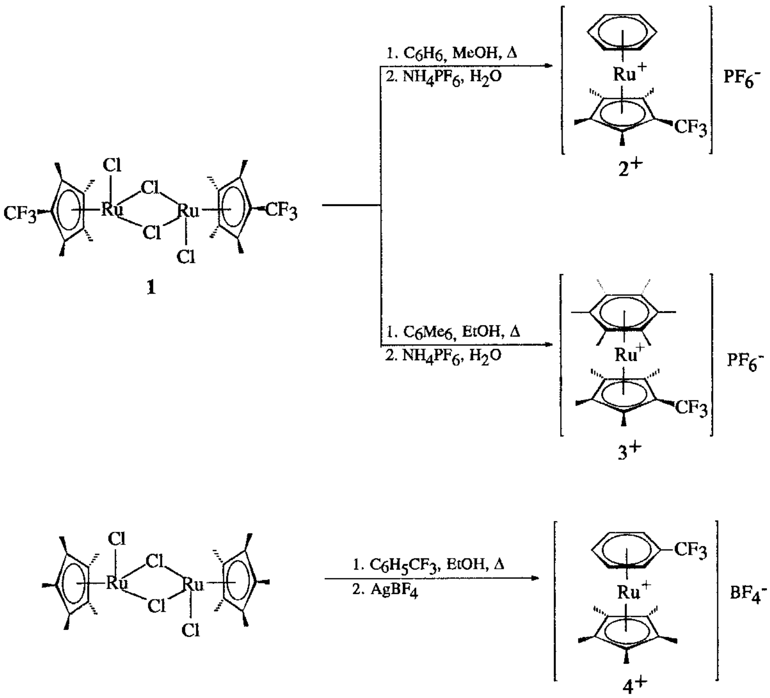
[2] The X-ray structure, ESR-spectroscopy and magnetochemistry data of $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) will be published in Inorg. Chim. Acta.



Scheme 2.

*2.3. Reduction of cationic complexes [Ru(η^5-$C_5Me_4CF_3$)(η^6-arene)]$^+$ (**2**$^+$, arene = C_6H_6; **3**$^+$, arene = C_6Me_6), and [Ru(η^5-C_5Me_5)(η^6-$C_6H_5CF_3$)]$^+$(**4**$^+$) with sodium amalgam*

The chemical reduction of **2**$^+$–**4**$^+$ was carried out in THF with an excess of 1% Na/Hg at ambient temperature.

The reduction of **2**$^+$–**3**$^+$ followed by the crystallization of neutral products from benzene led to dimers $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{–}\eta^5{:}\eta^5\text{-}C_6H_6C_6H_6)]$ (**5**) and $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{–}\eta^5{:}\eta^5\text{-}C_6Me_6C_6Me_6)]$ (**6**) in 69% and 61% yields respectively (Scheme 3).

The microanalysis and NMR spectroscopy data of dimers **5** and **6** are given in Tables 1–3.

The dimer **6** was obtained as a sole product. In the case of the reduction of **2**$^+$, two more neutral complexes were detected in mother liquors along with the dimer **5**. The presence of η^5-$C_5Me_4CF_3$ ligand in the second reduction product was confirmed by the appearance of two signals at δ 1.55 and 1.95 ($J_{H-F} = 1$ Hz) ppm in ^{1}H NMR spectrum as well as the signal at δ

Table 2
^{1}H and ^{19}F NMR data for complexes **2**$^+$–**6** (δ (Hz), reference to TMS)

Complex	Solvent	^{1}H NMR			^{19}F NMR
		η^5-C_5Me_5R	η^6-arene	μ-$\eta^5{:}\eta^5$-$C_6R'_6C_6R'_6$	
2$^+$, R = CF_3	acetone-d_6	2.17 (s, 6H, 2Me); 2.21 (q, 6H, 2Me, $J_{H-F} = 1.2$)	6.34 (s, 6H, C_6H_6)		6.2 (d, 6F, PF_6, $J_{F-P} = 708.1$); 23.8 (s, CF_3)
3$^+$, R = CF_3	acetone-d_6	1.83 (s, 6H, 2Me); 1.92 (q, 6H, 2Me, $J_{H-F} = 1.1$)	2.28 (s, 18H, C_6Me_6)		6.2 (d, 6F, PF_6, $J_{F-P} = 709.2$); 22.9(s, CF_3)
4$^+$, R = Me	acetone-d_6	2.07 (s, 15H, C_5Me_5)	6.3–6.7 (m, 5H, $C_6H_5CF_3$)		16.6 (s, CF_3); 72.9 (s, BF_4)
5, R = CF_3, R′ = H	C_6D_6	1.61 (s, 12H, 4Me); 1.95 (q, 12H, 4Me, $J_{H-F} = 1.0$)		1.70 (m, 2H); 2.62 (m, 4H); 4.12 (m, 4H); 5.21 (m, 2H)	25.5 (s, CF_3)
6, R = CF_3, R′ = Me	C_6D_6	1.52 (s, 12H, 4Me); 1.72 (s, 12H, 4Me)		1.03 (s, 6H, 2Me); 1.21 (s, 12H, 4Me); 1.72 (s, 12H, 4Me);	24.0 (s, CF_3)
2.10 (s, 6H, 2Me)	24.0 (s, CF_3)				

Table 3
^{13}C NMR data for complexes **2^+–6** (δ (Hz), reference to TMS)

Complex	Solvent	^{13}C NMR		
		η^5-C_5Me_5R	η^6-arene	μ–η^5:η^5-$C_6R'_6C_6R'_6$
2^+, $R = CF_3$	acetone-d_6	10.6 ($C_5\mathit{Me}_4CF_3$); 11.0 (q, $C_5\mathit{Me}_4CF_3$, $J_{C-F} = 2.3$); 86.5 (q, C–CF_3, $J_{C-F} = 36.8$); 96.1 ($\mathit{C}_5Me_4CF_3$); 100.4 ($\mathit{C}_5Me_4CF_3$); 126.2 (q, C–$\mathit{C}F_3$, $J_{C-F} = 271.6$)	89.9 (C_6H_6)	
3^+, $R = CF_3$	acetone-d_6 9.1 (q, $C_5\mathit{Me}_4CF_3$,	8.7 ($C_5\mathit{Me}_4CF_3$); $J_{C-F} = 2.2$); 84.5 (q, C–CF_3, $J_{C-F} = 36.4$); 91.8 ($\mathit{C}_5Me_4CF_3$); 95.8 ($\mathit{C}_5Me_4CF_3$); 126.5 (q, C–$\mathit{C}F_3$, $J_{C-F} = 271.5$)	15.8 ($C_6\mathit{Me}_6$); 101.6 (C_6Me_6);	
4^+, $R = Me$	acetone-d_6	9.8 ($C_5\mathit{Me}_5$); 99.2 (C_5Me_5)	84.1 (CH); 87.9 (CH); 89.6 (CH); 91.5 (q, C–CF_3, $J_{C-F} = 36.5$); 124.0 (q, C–CF_3, $J_{C-F} = 273.9$)	
5, $R = CF_3$, $R' = H$	C_6D_6	10.9 ($C_5\mathit{Me}_4CF_3$); 11.4 (q, $C_5\mathit{Me}_4CF_3$, $J_{C-F} = 1.9$); 75.4 (q, C–CF_3, $J_{C-F} = 37.0$); 81.4 ($\mathit{C}_5Me_4CF_3$); 88.2 ($\mathit{C}_5Me_4CF_3$); 131.7 (q, C–$\mathit{C}F_3$, $J_{C-F} = 274.3$)	80.9 (CH); 92.0 (CH)	35.2 (CH); 49.7 (CH);
6, $R = CF_3$, $R' = Me$	$CDCl_3$	9.0 ($C_5\mathit{Me}_4CF_3$); 9.3 (q, $C_5\mathit{Me}_4CF_3$, $J_{C-F} = 2.3$); 78.3 (q, C–CF_3, $J_{C-F} = 31.5$); 85.6 ($\mathit{C}_5Me_4CF_3$); 89.9 ($\mathit{C}_5Me_4CF_3$); 127.3 (q, C–$\mathit{C}F_3$, $J_{C-F} = 272.1$)		15.6 ($C_6\mathit{Me}_6$); 16.3 ($C_6\mathit{Me}_6$); 18.2 ($C_6\mathit{Me}_6$); 24.2 ($C_6\mathit{Me}_6$); 90.6 (C_6Me_6); 98.8 (C_6Me_6); 100.5 (C_6Me_6); 101.0 (C_6Me_6)

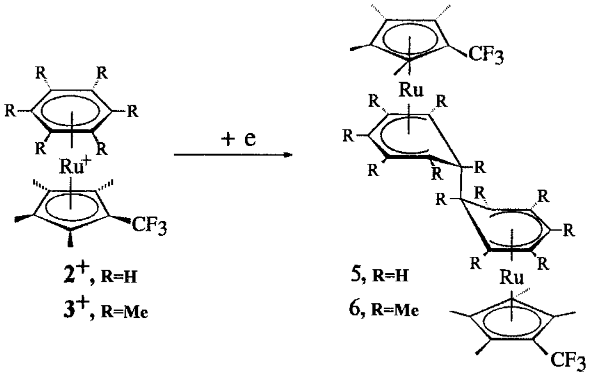
25.5 ppm in ^{19}F NMR spectrum. The ^{1}H NMR spectrum additionally contained three multiplets at δ 2.54, 4.12 and 5.04 ppm of the pattern characteristic for η^5-cyclohexadienyl derivatives. Unfortunately, the fourth resonance arising from cyclohexadienyl moiety, probably located in the region of δ 1.5–2.1 ppm, was masked by other signals thus giving no possibility to conclude whether the second compound is the cyclohexadienyl complex $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^5\text{-}C_6H_7)]$ or not.

The third product appeared as three narrow singlets at δ 1.68, 2.04 and 4.73 ppm in a ratio 6:6:6 in ^{1}H NMR spectrum. The downfield shifted singlet seems to arise from η^6-C_6H_6 ring bearing neutral organoruthenium fragment while the two upfield shifted singlets belong to unequivalent pairs of Me substituents in the η^4-$C_5Me_4CF_3$ ligand. In ^{19}F NMR spectrum, the resonance of trifluoromethyl group was slightly upfield shifted (δ 17.5 ppm) in comparison with two other products. This can be stipulated by the location of CF_3

Table 4
Cyclic voltammetry data for cationic sandwich complexes (carbonglass electrode, $c = 2 \times 10^{-3}$ mol l^{-1}; CH_3CN, 0.1 M Bu_4NBF_4; $\nu = 200$ mV s^{-1}; reference electrode SCE)

Complex	E_{pc} (V)	Complex	E_{pc} (V)	Complex	E_{pc} (V)
$[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]^+$	−1.97	$[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6Me_6)]^+$	−2.12	$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+$	−1.88
$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$	−2.02[a]	$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$	−2.18[a]	$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$	−2.32[a]
$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$	−2.32[a]	$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$	−2.51[a]	$[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Me)]^+$	−2.24

[a] Refs. [5,7].



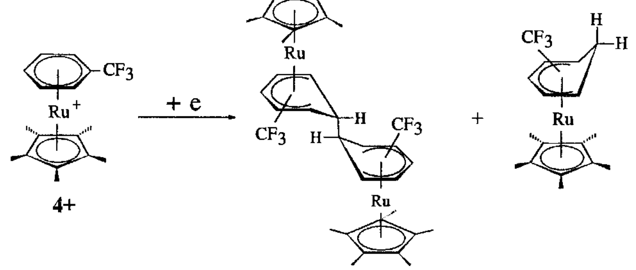
Scheme 3.

group at sp^3-carbon atom of η^4-$C_5Me_4CF_3$ ligand. The data obtained allow us to suppose the third product to be either the diene complex [Ru(η^4-$C_5Me_4CF_3H$)(η^6-C_6H_6)] or the dimer [Ru_2(η^6-C_6H_6)$_2$(μ–η^4:η^4-$C_5Me_4CF_3C_5Me_4CF_3$)].

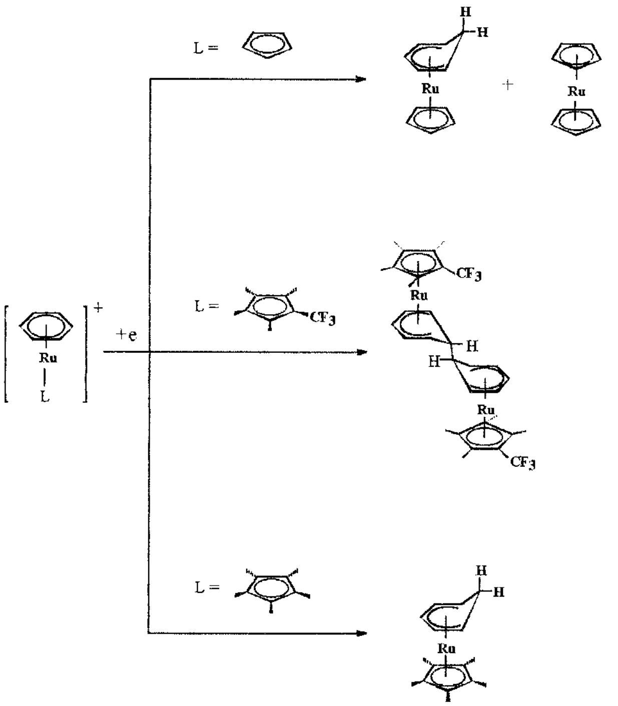
It should be outlined that the summary content of the two minor products in the reaction mixture was about 10%. Their high solubility in common organic solvents precluded the separation of either of them in an individual state.

The reduction of **4**$^+$ was non-selective and resulted in the formation of non-identifiable mixture of neutral products. At least 10 resonances of various intensities were observed in a region of δ 8–18 ppm in ^{19}F NMR spectrum of this mixture. As there are four positions in η^6-$C_6H_5CF_3$ ligand able to participate in both H-atom addition and dimerization, one can expect a formation of four mononuclear cyclohexadienyl complexes [Ru(η^5-C_5Me_5)(η^5-$C_6H_5CF_3H$)] and of 10 dimers [Ru_2(η^5-C_5Me_5)$_2$(μ–η^5:η^5-$C_6H_5CF_3C_6H_5CF_3$)] on the reduction of **4**$^+$. Attempts to separate this complicated mixture were unsuccessful (Scheme 4).

The reduction of **2**$^+$ leading to the formation of dimer **5** differs from the reduction of cyclopentadienyl analogue [Ru(η^5-C_5H_5)(η^6-C_6H_6)]$^+$ resulting in a mixture of cyclohexadienyl complex [Ru(η^5-C_5H_5)(η^5-C_6H_7)] and ruthenocene [5,7]. The reduction of pentamethylcyclopentadienyl analogue [Ru(η^5-C_5Me_5)(η^6-C_6H_6)]$^+$ gave the complex [Ru(η^5-C_5Me_5)(η^5-C_6H_7)] as the only product [5,7] (Scheme 5).

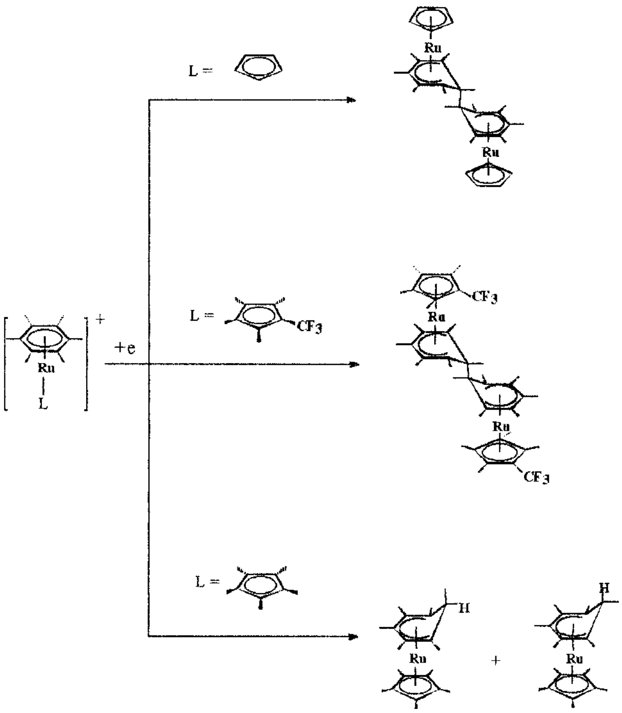


Scheme 4.



Scheme 5.

The formation of dimers [Ru_2(η^5-$C_5Me_4CF_3$)$_2$(μ–η^5:η^5-$C_6Me_6C_6Me_6$)] (**6**) and [Ru_2(η^5-C_5H_5)$_2$(μ–η^5:η^5-$C_6Me_6C_6Me_6$)] [5,7] was observed on the reduction of **3**$^+$ and [Ru(η^5-C_5H_5)(η^6-C_6Me_6)]$^+$ respectively. H-atom addition products [Ru(η^5-C_5Me_5)(η^5-C_6Me_6H)] as a mixture of *endo*-H and *exo*-H isomers



Scheme 6.

were obtained on the reduction of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$ under the same conditions [5,7] (Scheme 6).

The examination of results obtained for the reduction of the two series of $[Ru(\eta^5\text{-}L)(\eta^6\text{-}C_6H_6)]^+$ and $[Ru(\eta^5\text{-}L)(\eta^6\text{-}C_6Me_6)]^+$ (L = C_5H_5, C_5Me_5, $C_5Me_4CF_3$) compounds reveals that the structure of reduction products is, to a great extent, governed by steric and electronic properties of cyclopentadienyl ligands. The pentamethylcyclopentadienyl complexes are only able to give cyclohexadienyl products $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_6R_6H)]$ (R = H, Me) by an H-atom addition, while $\eta^5\text{-}C_5Me_4CF_3$ complexes form the dimers $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_6R_6C_6R_6)]$ (R = H, Me). Taking into account that $\eta^5\text{-}C_5Me_5$ and $\eta^5\text{-}C_5Me_4CF_3$ ligands are similar in their steric bulk, one could suggest that the different behavior of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6R_6)]^+$ and $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6R_6)]^+$ (R = H, Me) complexes in reduction processes is stipulated by the lower electron-donor ability of $\eta^5\text{-}C_5Me_4CF_3$ ligand in comparison with $\eta^5\text{-}C_5Me_5$ ligand. Probably, the additional electron-donor effect of pentamethylcyclopentadienyl ligand makes the 19-electron radicals $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6R_6)]$ (R = H, Me) to become more reactive than $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6R_6)]$ analogues and the H-atom abstraction from the solvent occurs rather than the dimerization of radicals through the arene rings.

The degree of steric protection exerted by both cyclopentadienyl and arene ligands is also very important for determining the outcome of 19-electron radical transformations. The sterically 'non-protected' $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ radical undergoes an easy decomposition and gives the H-atom addition and disproportionation products in low yields. At the same time, the $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]$ radical containing $\eta^5\text{-}C_5Me_4CF_3$ ligand, which is very similar to cyclopentadienyl ring in its electronic influence, gives the corresponding dimer $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_6R_6C_6H_6)]$ as the highly predominate product. The increase in the stability of 19-electron $[Ru(\eta^5\text{-}L)(\eta^6\text{-}C_6Me_6)]$ (L = C_5H_5, $C_5Me_4CF_3$) radicals leads to the formation of corresponding dimers on the reduction of their 18-electron cationic precursors.

3. Conclusions

It can be summarized that ligands stabilize 19-electron radical either by making metal centers more sterically protected (steric stabilization) or by delocalizing unpaired electron density (electronic stabilization). Among the ruthenium arenecyclopentadienyl radicals containing monocyclic arene and cyclopentadienyl ligands, the 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadienyl radicals $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-arene})]$ (arene = C_6H_6, C_6Me_6) studied here appear to be the most kinetically stable undergoing dimerization through arene ligand rather than H-atom addition. This can be accounted for by optimum ratio of electronic and steric stabilization that is specific for $\eta^5\text{-}C_5Me_4CF_3$ ligand. The lower stability of cyclopentadienyl $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]$ and pentamethylcyclopentadienyl $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-arene})]$ (arene = C_6H_6, C_6Me_6) radicals is caused by decreased steric and electronic stabilization respectively.

4. Experimental details

Reactions were carried out under argon, using standard Schlenk-line techniques. Solvents and reagents were purified and dried by standard methods and were distilled under argon immediately prior to use. The 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene was synthesized as described in Ref. [16]. Cationic complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Me)]^+$ for CV measurements was prepared by literature method [21]. Microanalyses were performed by the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Table 1).

The ^1H, ^{19}F and ^{13}C NMR spectra were obtained with Bruker WP-200SY and Bruker-AMX-400 spectrometers in acetone-d_6, $CDCl_3$ and C_6D_6 solutions. All chemical shifts (δ) are reported in ppm with reference to TMS (Tables 2 and 3).

CV data were obtained in acetonitrile solutions at room temperature under argon using potentiostat PI-50-1. A three-electrode cell was used with SCE reference electrode, a carbonglass working electrode and a platinum auxiliary electrode. The scan rate was 200 mV s^{-1} in each case. The solutions of electroactive substance were 2×10^{-3} mol l^{-1} in 0.1 M Bu_4NPF_6 as the supporting electrolyte. Peak potentials were calibrated against the ferrocene/ferrocenium (0.40 V) couple by adding ferrocene directly to the solution containing ruthenium complexes under investigation. Peak potentials are reported vs. SCE in Table 4.

Bulk electrolyses were carried out in THF solutions under argon using potentiostat P-5827M. Working stirred mercury cathode of 11 cm^2 area was separated from platinum counterelectrode by a frit G4. An aqueous SCE served as reference electrode, which had the KCl phase separated from the solution by a frit G4. A solution of supported electrolyte had been electrolyzed at the same potential, which was chosen for compound studied, before ruthenium complex was dissolved. Coulometry measurements were made with a OH-404 'Radelkis'.

*4.1. Synthesis of $[Ru_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**)*

$RuCl_3 \cdot (H_2O)_3$ (2.0 g, 7.65 mmol) was refluxed in EtOH (40 ml) with an excess of $C_5Me_4CF_3H$ (3.8 g, 20.0 mmol) to give, after 2 h, a brown precipitate of **1**.

The reaction mixture was concentrated and filtered. The microcrystalline solid was then washed by hexane and dried in vacuo. The resulting product was recrystallized from CH_2Cl_2/Et_2O to give the dark brown crystals. ^1H NMR ($CDCl_3$): δ −1.53 (s, 6H, 2Me); 12.70 (s, 6H, 2Me) ppm. ^{19}F NMR (C_6D_6): δ 39.0 (CF_3) ppm.

*4.2. Synthesis of $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**2^+**) and $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ (**3^+**) (general procedure)*

The dimer **1** (0.20 g, 0.28 mmol) in methanol (20 cm^3) was heated under reflux with an excess of benzene (1.1 cm^3, 12.5 mmol) for 2 h. After the color turned from green to red-yellow, the solution was evaporated and the residue was washed by Et_2O and dried. Solid was further dissolved in water and filtered. The filtrate was treated with an excess of NH_4PF_6 precipitating $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**2^+**) as a white or pale yellow solid. The latter was then dissolved in acetone and eluted through a short Al_2O_3 column. After concentration, the solution was treated with Et_2O resulting in a white crystalline precipitate of **2^+**.

$[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ (**3^+**) was prepared analogously in refluxing ethanol.

*4.3. Synthesis of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+BF_4^-$ (**4^+**)*

$[Ru_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)_2]$ (0.30 g, 0.50 mmol) was refluxed in ethanol (15 cm^3) with an excess of α,α,α-trifluorotoluene (2.7 cm^3, 22.5 mmol) for 2 h, and then stirred with $AgBF_4$ for 1 h at room temperature. The precipitate of AgCl was filtered off and washed by CH_2Cl_2. The filtrate was evaporated, residue was then dissolved in acetone and eluted through a short Al_2O_3 column. After concentration, the solution was treated with Et_2O resulting in a white crystalline precipitate of **4^+**.

*4.4. Reduction of $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**2^+**), $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6 - C_6Me_6)]^+PF_6^-$ (**3^+**) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+BF_4^-$ (**4^+**) (general procedure)*

Suspension of **2^+** (0.17 g, 0.33 mmol) in THF (30 cm^3) was stirred with an excess of 1% Na/Hg (2 h, 25°C). The solution was decanted, filtered and the solvent was removed in vacuo, to leave a residue which was extracted by benzene (3×10 cm^3). Combined benzene solutions were filtered, evaporated to dryness and the residue was crystallized from hexane to give **5**. The complexes **3^+**–**4^+** were reduced analogously.

*4.5. Bulk electrolysis of $[Ru(\eta^5\text{-}C_5Me_4CF_3)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**2^+**)*

Complex **2^+** (0.05 g, 0.10 mmol) was reduced in 0.1 M Bu_4NPF_6 solution in THF (50 cm^3) at −2.1 V; using carbonglass electrode; after consumption of $Q = 10.8$ ($Q_{theor} = 9.8$, $n = 1$) the current decreased from 15 to 2 mA and electrolysis was stopped. Cyclic voltammogram of the resultant solution showed the absence of cathodic peak at −1.97 V (**2^+**) and new oxidation peak at +0.26 V was observed in the anodic branch of the CV curve. The oxidation of the solution obtained at +0.5 V ($Q_{exp} = 9.0$) led to the regeneration of **2^+** ($E_{pc} = -1.97$ V).

*4.6. Bulk electrolysis of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5CF_3)]^+BF_4^-$ (**4^+**)*

Complex **4^+** (0.05 g, 0.10 mmol) was reduced in 0.1 M Bu_4NPF_6 solution in THF (50 cm^3) at −2.0 V, using carbonglass electrode; after consumption of $Q = 9.5$ ($Q_{theor} = 9.7$, $n = 1$) the current decreased from 9 to 2 mA and electrolysis was stopped. The cyclic voltammogram of resultant solution showed the absence of cathodic peak at −1.88 V (**4^+**) and new oxidation peak at +0.19 V was observed in the anodic branch of the CV curve. The oxidation of the solution obtained at +0.5 V ($Q_{exp} = 9.1$) led to the regeneration of **4^+** ($E_{pc} = -1.88$ V).

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