IMPROVED METHOD FOR SYNTHESIS OF ARENECYCLOPENTADIENYLRUTHENIUM CATIONS

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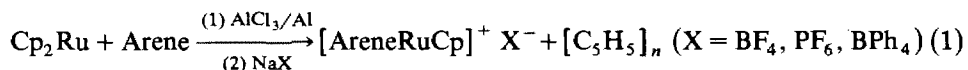
Summary

An improved method for the synthesis of [AreneRuCp]$^+$ salts by means of ligand exchange at ruthenocene is described.

A set of new [AreneRuCp]$^+$X$^-$ was obtained. The ^{1}H NMR spectra of arenecyclopentadienylruthenium salts were discussed.

Introduction

Earlier we described [1,2] the ability of ruthenocene and substituted ruthenocene to exchange one cyclopentadienyl ligand for various arenes and thus to form cationic arenecyclopentadienylruthenium derivatives.

$$Cp_2Ru + Arene \xrightarrow[\text{(2) NaX}]{\text{(1) AlCl}_3/\text{Al}} [AreneRuCp]^+ X^- + [C_5H_5]_n \quad (X = BF_4, PF_6, BPh_4) \quad (1)$$

This reaction may be considered as a method for the synthesis of cationic arenecyclopentadienylruthenium derivatives containing various substituents in the ligands. However, in contrast to ferrocene, ruthenocene exchanges its cyclopentadienyl ligand for an arene with much more difficulty. Thus, low yields (3–7%) of the [AreneRuCp]$^+$ salts result. Ref. 3 describes the interaction of ruthenocene with mesitylene and hexamethylbenzene in the presence of AlCl$_3$/Al/H$_2$O, product yields being 30 and 50%, respectively. In these conditions, however, considerable dealkylation of alkylarenes was observed. Later another method [4] for the synthesis of the salts of [AreneRuCp]$^+$ by means of the action of C$_5$H$_5$Tl upon dimers [AreneRuCl$_2$]$_2$ was proposed. Yields were between 47 and 82%, but in each case it was necessary to synthesize the initial [AreneRuCl$_2$]$_2$ by the action of RuCl$_3$ upon the corresponding 1,3- or 1,4-cyclohexadiene [4,5].

TABLE 1

CONDITIONS FOR THE SYNTHESIS OF [AreneRuC5H5]+ X− a

Arene	Ratio of reagents [b]	Reaction conditions (°C/h)	Yield, (%)	M.p. (dec. p.) (°C)	Analysis (Found (calc.)(%)) C	H
C_6H_6	1/3/1	125–130/10–12	66	–	39.72 (39.89)	3.35 (3.30)
$CH_3C_6H_5$	1/3/0.2	125/13	66	260—262	(see [1])	
$C_2H_5C_6H_5$	1/3/1	140–150/15	25	251–252	mixture	
$C_6(CH_3)_6$ [c]	1/2/1 [d]	130/10	25	decomposes gradually	48.54 (48.89)	5.47 (5.56)
Phenanthrene [c]	1/3/1 [d]	100–110/12	0.4	132–140	–	–
Naphthalene [c]	1/3/1 [d]	125–130/15	13	125–130	–	–
ClC_6H_5 [e]	1/3/0.3	125/14	40	209–212	(see [1])	
FC_6H_5	1/4/0	105–110/7	13	305–307	37.83 (37.84)	3.08 (2.88)
	1/3/0	125/14	23		F, 26.77 (27.21)	
$CH_3OC_6H_5$ [c]	1/3/2 [f]	115–125/6 [f]	1.1	126–132	(see [6])	

a $X = BF_4$, except the reaction with $C_2H_5C_6H_5$, where $X = PF_6$. b $(C_5H_5)_2Ru/AlCl_3/Al$; H_2O was added in the amount of 1–5 drops except the reaction with $C_2H_5C_6H_5$; arene was in excess and served as a solvent. c In these experiments the following solvents were employed: for $C_6(CH_3)_6$, octane; for phenanthrene and naphthalene, heptane; for $CH_3OC_6H_5$, nonane. d $(C_5H_5)_2Ru$/naphthalene 1/1.8; $(C_5H_5)_2Ru$/phenanthrene or $C_6(CH_3)_6$ 1/2. e $[ClC_6H_5RuC_5H_5]PF_6$ was obtained by exchange of anion from $[ClC_6H_5RuC_5H_5]BF_4$. An analytical sample was obtained after reprecipitation from dichloroethane by abs. ether. M.p. 241—243°C (dec.). Found: C, 31.35; H, 2.48; P, 7.28. $C_{11}H_{10}RuClF_6P$ calcd.: C, 31.17; H, 2.38; P, 7.31%. f The experiment was carried out under atmospheric pressure.

Results and discussion

In the present paper we describe an improved method for the synthesis of [AreneRuCp]$^+$ X$^-$ from ruthenocene as well as a number of new arenecyclopentadienylruthenium cations. While carrying out reaction 1 in an autoclave at higher temperatures we obtained good yields of [AreneRuCp]$^+$ salts (see Table 1). In most experiments a few drops of water were added to the reaction mixture. This procedure promotes the substitution of one Cp ring at Cp$_2$Fe and Cp$_2$Ru [3,7]. Contrary to the data given in ref. 3, appropriate conditions were chosen to avoid dealkylation of such ligands as CH$_3$C$_6$H$_5$, and, (CH$_3$)$_6$C$_6$. ^{1}H NMR spectra were employed for monitoring the process. The only exception was an experiment with ethylbenzene where the signal of the Cp group in the ^{1}H NMR spectrum was split into two signals with δ 5.44 and 5.51 ppm. The signal of the arene protons appears to be a multiplet with the centre at 6.27 ppm, the signals of CH$_2$ and CH$_3$ groups are singlets at 1.40 and 1.29 ppm, respectively. The nature of the signals of cyclopentadienyl and arene protons suggests the formation of a [C$_6$H$_6$RuCp]PF$_6$/[C$_2$H$_5$C$_6$H$_5$RuCp]PF$_6$ mixture. The chromatogram on Al$_2$O$_3$ (the eluent is dichloroethane/alcohol) also proves the presence of the two substances in the product.

Almost all the arenecyclopentadienylruthenium tetrafluoroborates obtained are pale-yellow or white crystalline compounds. The naphthalene derivative is orange-brown, while the phenanthrene derivative is brown. The arenecyclopentadienylruthenium tetrafluoroborates are soluble in water, ethanol, dichloroethane, acetone and acetonitrile. Hexafluorophosphates are less soluble than tetrafluoroborates.

All the cationic arenecyclopentadienylruthenium derivatives thus obtained were characterized by IR and ^{1}H NMR spectra. Table 2 shows the ^{1}H NMR spectra of all the [AreneRuCp]$^+$ X$^-$ described hitherto. The parameters of the spectra of the corresponding iron derivatives are given in Table 3.

The analysis of the data given in Table 2 and their comparison with those given in Table 3 show that the spectra of all [AreneRuCp]$^+$ X$^-$ are very similar to the spectra of all [AreneFeCp]$^+$ X$^-$, which have already been reported in the preliminary paper [1]. The downfield shift of the Cp protons relative to the signal of Cp protons of ruthenocene is observed in all [AreneRuCp]$^+$ X$^-$ spectra. The shift is weaker in this case as compared with the cases for the corresponding derivatives of iron. Thus, for [C$_6$H$_6$RuC$_5$H$_5$]$^+$ the shift is 0.85 ppm, while for [C$_6$H$_6$FeC$_5$H$_5$]$^+$ it is 1.03 ppm. The downfield shift of the Cp ligand protons relative to the Cp$_2$Fe spectrum was explained for the arenecyclopentadienyliron cations [14] as being due to delocalization of the positive charge of the cationic π-complex on the ligands. This explanation would seem to be applicable for the ruthenium derivatives also, though in this case delocalization of the positive charge is weaker than for [AreneFeCp]$^+$.

The signal of the benzene ligand protons in the spectrum of [C$_6$H$_6$RuCp]$^+$ is shifted upfield by 1.07 ppm as compared with the proton signal for non-coordinated benzene. The corresponding value for the iron derivative is somewhat less (0.83 ppm [14]). The same shift is observed for all other [AreneRuCp]$^+$ cations. The upfield shift for Arene = CH$_3$C$_6$H$_5$ is 0.91 ppm; Arene = CH$_3$OC$_6$H$_5$, 0.83 ppm, etc. (the data for non-coordinated arenes are taken from ref. 8). The upfield shift of coordinated arene protons is a well-known phenomenon [15]. It seems to depend upon a change in the electron density on the aromatic ligand [16]. This is confirmed

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TABLE 2

^{1}H NMR SPECTRA OF [AreneRuCp]$^+$ SALTS

Substance	δ(Cp), (ppm)	δ(Arene), (ppm)	δ(Substituent) (ppm)	References
C_6H_6			7.27s(6)	8
$(C_5H_5)_2Ru$	4.60s(5)			1
$[C_6H_6RuCp]PF_6$	5.45s(5)	6.20s(6)		1
$[C_6H_6RuCp]BF_4$	5.56s(5)	6.33s(6)		This work
$[MeC_6H_5RuCp]BF_4$	5.45s(5)	6.16br s(6)	2.43s(3)	1
$[Me_3C_6H_3RuCp]BF_4$	5.31s	6.18	2.36s	3
$[(p\text{-}MeC_6H_4CHMe_2)RuCp]BPh_4$ ^{a}	5.31s(5)	6.11s(4)	2.22s(Me,3)	4
			1.15d(2Me,6)	
$[Me_6C_6RuCp]BF_4$ ^{b}	5.20s(5)		2.49s(18)	This work
$[PhC_6H_5RuCp]PF_6$	5.49s(5)	6.34–6.85m(5)	7.34–7.87m(5)	1
$[C_{10}H_8RuC_5H_5]BF_4$	5.15s(5)	6.45s(2)	7.70–7.82m(4)	This work
		7.24s(2)	7.70–7.82m(4)	This work
$[C_{14}H_{10}RuCp]BF_4$	5.11s(5)	^{c}	^{c}	This work
$[ClC_6H_5RuCp]BF_4$	5.71s(5)	6.36–6.69m(3)		
		6.76–6.98m(2)		1
$[FC_6H_5RuCp]BF_4$	5.64s(5)	6.18–6.58m(3)		This work
		6.71–6.93m(2)		
$[MeOC_6H_5RuCp]BF_4$	5.51s(5)	6.13–6.53m(5)	3.90s(3)	6
$[H_2NC_6H_5RuCp]BF_4$	5.38s(5)	6.13m(5)	5.93m(NH$_2$)	6
$[C_5H_{10}NC_6H_5RuCp]BF_4$	5.46s(5)	6.13s(5)	1.69br s H$_2$C(CH$_2$)$_2$	6
			3.29br s N(CH$_2$)$_2$	
$[HOOCC_6H_5RuCp]PF_6$	5.65s(5)	6.62d(3)		10
		6.92d(2)		
$[PhSC_6H_5RuCp]PF_6$	5.60s(5)	6.35s(5)	7.67s(5)	10
$[C_6H_6RuC_5H_4Et]PF_6$	5.56s(2)	6.36s(6)	2.42q(CH$_2$)	2
	5.44s(2)		1.13t(CH$_3$)	
$[Me_3C_6H_3RuC_5H_4Et]PF_6$	5.37t(2)	6.29s(3)	2.6s(CH$_2$ + 3CH$_3$,11)	2
	5.31t(2)		1.24s(CH$_3$,3)	
$[ClC_6H_5RuC_5H_4COMe]PF_6$	6.10s(2)	6.88–6.40(5)	2.44(CH$_3$,3)	2
	5.80s(2)			

^{a} Solvent $(CD_3)_2SO$; δ(BPh$_4$) 6.60–7.60 ppm. ^{b} Literature data for [Me$_6$C$_6$RuCp]BF$_4$: δ(Cp) 5.30; (6Me) 2.50 ppm [3]. ^{c} ^{1}H NMR spectrum of the arene ligand in the phenanthrene derivative: δ (H(2,3)) 6.40–6.73 t (2); (H(1)) 7.06–7.24 t (1) (coordinated ring), (H(4) and H(6–10)) 7.51–8.08m(6); (H(5)) 8.56–8.84 q (1) ppm.

by the values of the shift for a number of arenecyclopentadienyl-transition metal derivatives of Groups VII and VIII. The upfield shift is especially strong for aromatic protons at the non-charged complexes $C_6H_6MC_5H_5$, M = Mn, Re (2.56 and 2.50 ppm, respectively [17]). The electron density on the arene ligands of these compounds is higher due to the back donation of electrons from the metal atom onto the arene ligand (the dative component of the bond). For the single-charged cations [AreneMCp]$^+$ (M = Fe, Ru) the shift is considerably less, which can be explained by partial delocalization of the positive charge on the arene ligand, see also ref. 14. The upfield shift of the signals for the arene ligand protons in the ^{1}H NMR spectra of the two-charged cations [AreneMC$_5$(CH$_3$)$_5$]$^{2+}$ (M = Ir, Rh) [18]) is absent, because it is suppressed by the powerful influence of the two positive charges.

Comparison of the shifts under consideration, [AreneFeCp]$^+$, 0.83 ppm and

TABLE 3

^{1}H NMR SPECTRA OF [AreneFeCp]$^+$ SALTS [a]

Substance	δ(Cp) (ppm)	δ(Arene) (ppm)	δ(Substituent) ppm	Ref.
$(C_5H_5)_2$Fe	4.20s(5)			1
[C_6H_6FeCp]PF$_6$	5.23s(5)	6.44s(6)		1
[MeC$_6$H$_5$FeCp]PF$_6$	5.27s(5)	6.56s(5)	2.56s(3)	1
[Me$_3$C$_6$H$_3$FeCp]BF$_4$	5.07s(5)	6.30s(3)	2.52s(9)	11
[Me$_6$C$_6$FeCp]BF$_4$	4.78s(5)		2.58s(18)	11
[C$_6$H$_5$C$_6$H$_5$FeCp]BF$_4$	5.14s(5)	6.51–7.09m(5)	7.42–8.11m(5)	1
[C$_{10}$H$_8$FeCp]PF$_6$	4.78s(5)	7.48m(2,α-H) 6.60m(2,β-H)	8.04(4, uncoord. ring)	12
[C$_{14}$H$_{10}$FeCp]PF$_6$	4.62s(5)	see [b]	see [b]	13
[ClC$_6$H$_5$FeCp]BF$_4$	5.40s(5)	6.54–7.07m(5) [c]		1
[FC$_6$H$_5$FeCp]PF$_6$	5.32s	6.63m		14
[CH$_3$OC$_6$H$_5$FeCp]PF$_6$	5.15s	6.33m	4.03	14
[H$_2$NC$_6$H$_5$FeCp]PF$_6$	4.95s	6.01m	5.67	14
[HOOCC$_6$H$_5$FeCp]PF$_6$	5.35s	6.78d(3) 7.10d(2)		10

[a] Conditions for obtaining the spectra see in the corresponding papers. [b] ^{1}H NMR spectra of the arene ligand in the phenanthrene derivative: δ(H(2,3)) 6.64m(2); (H(1)) 7.25m(1); (coord. ring); (H(4,6–10)) 8.00m(6); (H(5)) 8.80m(1) ppm. [c] Two overlapping multiplets.

[AreneRuCp]$^+$, 1.07 ppm shows that the positive charge in the ruthenium cation influences the arene ligand to a lesser extent than it does in the iron cation. These data agree closely with the preliminary conclusions made earlier which were based on a comparison of the reactivity of [ClC$_6$H$_5$FeC$_5$H$_5$]$^+$ with [ClC$_6$H$_5$RuC$_5$H$_5$]$^+$ [6]. Therefore, on passing from iron to ruthenium the influence of the positive charge upon both ligands becomes less. The same assumption which describes a decreasing rate of delocalization of the positive charge on the arene ligand in [AreneMCp]$^+$: Fe > Ru > Os, is reported in ref. 4.

An increase in electron density on the coordinated arene upon passing from iron complexes to complexes of ruthenium and osmium is not unique for [AreneMCp]$^+$. The electrophilic reactivity of [$(C_6H_6)_2$M]$^{2+}$ (M = Fe, Ru, Os) decreases with respect to nucleophiles R$_3$P in the series Fe ≫ Ru > Os [19]. The authors attribute this phenomenon to an increase in the electron density on the arene ligands due to an increase on the part of the dative component in the arene–metal bond on passing from iron to ruthenium and osmium.

^{19}F NMR spectra were recorded for compounds [FC$_6$H$_5$FeC$_5$H$_5$]BF$_4$ and [FC$_6$H$_5$RuC$_5$H$_5$]BF$_4$. Upfield shifts of the signals for fluorine by 21.73 and 23.18 ppm, respectively, were observed with regard to the signal of fluorine in non-coordinated fluorobenzene. Therefore, the ^{19}F NMR spectra confirm the conclusion, based on the comparison of ^{1}H NMR spectra of cationic arenecyclopentadienyl complexes of iron and ruthenium, that the positive charge influences the arene ligand to a lesser extent in the ruthenium than in the corresponding iron complexes.

IR spectra were recorded for all [AreneRuCp]$^+$ salts. They were found to be very similar to those of the corresponding [AreneFeCp]$^+$.

IR spectra of [AreneRuCp]$^+$ BF$_4^-$ (cm^{-1}):

$[C_6H_6RuC_5H_5]BF_4$: 3065s, 1410s, 1300w, 1020–1120 plateau, 860m, 825s, 570m, 545m.

$[CH_3C_6H_5RuC_5H_5]PF_6$: 3130m, 2950w, 1540w, 1470m, 1420m, 1390m, 1160w, 1110w, 1075, 1055 and 1010w, 830–860s, 790m, 560s, 430m.

$[(CH_3)_6C_6RuC_5H_5]BF_4$: 3015–3030m, 1458m, 1415m, 1395m, 1290–1310w, 1030–1090s, 845m, 540m, 525m, 430s.

$[(Phenanthrene)RuC_5H_5]BF_4$: 3425 plateau, 3065m, 1610w, 1410m, 1040–1125s, pl., 840m, 760m.

$[(Naphthalene)RuC_5H_5]BF_4$: 3400 plateau, 3060–3070s, 2065w, 2000w, 1665m, 1440m, 1415m, 1300w, 1020–1100 pl., 860m, 825m, 570m, 550m.

$[ClC_6H_5RuC_5H_5]BF_4$: 3390–3480s, 3060–3090m, 1790w, 1630–1650w, 1500m, 1430m, 1420m, 1300w, 1020–1120s, 860m, 840m, 700m, 540m, 525m, 450m.

$[ClC_6H_5RuC_5H_5]PF_6$: 3120m, 3100m, 1500m, 1430m, 1415m, 1090m, 1010w, 915m, 830–860s, 700m, 560s, 450m.

$[FC_6H_5RuC_5H_5]BF_4$: 3360–3560m, 3060s, 1520s, 1450s, 1410s, 1230s, 1020–1100s, 840s, 800s, 535w, 515s, 455s, 425m, 400m.

$[CH_3OC_6H_5RuC_5H_5]BF_4$: 3400m, 3060m, 1525s, 1465m, 1440s, 1410m, 1260s, 1020–1120s, 840m, 780m, 660m, 560m, 535m, 520m, 470m.

$[C_5H_{10}NC_6H_5RuC_5H_5]BF_4$: 3070s, 2940s, 2840–2860m, 1650w, 1540s, 1470m, 1410m, 1360m, 1275w, 1250s, 1220w, 1020–1100s, 910w, 860w, 840m, 720w, 665m, 535w, 525w, 500w, 475m, 430m, 420m.

$[H_2NC_6H_5RuC_5H_5]BF_4$: 3340m, 3280m, 3160m, 3070w, 1630s, 1560s, 1480s, 1440w, 1420m, 1300s, 1020–1120s, 840s, 820w, 800m, 665m, 535m, 525m, 450w, 425m.

$[C_6H_6RuC_5H_4C_2H_5]PF_6$: 3130m, 3100m, 2990m, 2950m, 2890w, 2050m, 2000w, 1490m, 1450s, 1320m, 1060w, 980w, 830–860s, 560s, 475m.

$[(CH_3)_3C_6H_3RuC_5H_4C_2H_5]PF_6$: 3100m, 2980m, 2940m, 2880w, 1540m, 1460m, 1390m, 1040m, 830–860s, 560s, 530w, 510w, 480w.

$[ClC_6H_5RuC_5H_4COCH_3]PF_6$: 3135m, 3110m, 3090m, 1700s, 1510w, 1450m, 1410m, 1390m, 1370m, 1280s, 1120m, 1110m, 920m, 860–830s, 720m, 650w, 565s, 525m, 410s.

$[HOC_6H_5RuC_5H_5]PF_6$: 3470w, 3030–3130s, 2775m, 2670m, 2570m, 2480w, 1540s, 1510s, 1470s, 1440s, 1420m, 1410w, 1340w, 1300w, 1270s, 1240s, 1150w, 1110w, 1040w, 1000w, 830–860s, 665m, 560s, 535m, 460m, 415–425s.

$[C_6H_5SC_6H_5RuC_5H_5]PF_6$: 3120–3140m, 2390w, 1600w, 1520w, 1500m, 1460s, 1430w, 1410w, 1300w, 1290w, 1200w, 1170w, 1090m, 1040w, 1020w, 840–860s, 780m, 750s, 710m, 655w, 565s, 480w, 460m, 435m, 410m.

$[NCC_6H_5RuC_5H_5]PF_6$: 3100–3120s, 2260w, 1340m, 1310m, 1010w, 920m, 830–860s, 780w, 765w, 560s, 435m.

$[HOOCC_6H_5RuC_5H_5]PF_6$: 3130m, 3100m, 2680w, 2570w, 1720s, 1520m, 1420s, 1300s, 1280m, 1150w, 1130m, 1050w, 1010w, 830–860s, 665m, 560s, 440s.

$[C_6H_5SO_2C_6H_5RuC_5H_5]PF_6$: 3110m, 1450w, 1420w, 1400w, 1340m, 1320w, 1290w, 1170s, 1100s, 1070w, 1010w, 920w, 830–860s, 780m, 740s, 700m, 590s, 575m, 560s.

In the present paper we also describe an improved laboratory procedure for the synthesis of ruthenocene. While elaborating the procedure, we followed the method proposed in ref. 22, which we modified. The procedure described herein allows the production of ruthenocene in large amounts and in much higher yields (95% instead of 75%).

Experimental

The reactions were carried out in an autoclave without filling it with argon. The IR spectra (KBr pellets) were recorded on an UR-20 spectrometer. The ^{1}H NMR spectra were recorded with Hitachi–Perkin–Elmer R-12 (60 MHz) and Bruker-SXP-4-100 instruments in hexadeuterioacetone with TMS as the internal standard. The ^{19}F NMR spectra were recorded with Tesla BS-497 instrument; the working frequency with respect to fluorine was 94.075 MHz.

Preparation of ruthenocene. A mixture of $RuCl_3$ (10 g, 0.05 mol) and 300 ml of absolute ethanol was stirred for 2–3 h at ~ 20°C. Then the freshly distilled cyclopentadiene was added to this mixture (35 ml, 0.4 mol). To the mixture obtained zinc powder (30 g, 0.5 mol) was added gradually in small portions in such a way that the temperature of the reaction mixture does not exceed 30–35°C. Then the mixture was stirred at 20°C for 3–4 days. A precipitate was filtered off and thoroughly washed with hot benzene on the filter. The combined filtrates were evaporated up to 10 ml under reduced pressure. This residue was passed through the column with SiO_2 (SiO_2 volume was 20–25 cm^3). Ruthenocene was eluated from SiO_2 by benzene. Thus was obtained 10 g (95%) of ruthenocene with m.p. 193–195°C. After recrystallization from hexane m.p. was 195–199°C (Lit. [22]: m.p. 199–200°C).

Preparation of benzene-cyclopentadienylruthenium tetrafluoroborate. A mixture of ruthenocene (1.15 g, 5 mmol), $AlCl_3$ (2 g, 15 mmol), Al powder (0.15 g, 5 mmol) and 25 ml of benzene containing 2 drops of water was heated in the autoclave upon stirring for 10–12 h at 125–130°C. Then the mixture was cooled up to 0°C and was gradually decomposed by pouring onto ice (25 g). The layers were separated, the water layer was neutralized with $NaHCO_3$ and an excess of $NaBF_4$ was added to this layer.

The mixture obtained was thoroughly extracted with dichloroethane, the extract was dried over Na_2SO_4 and concentrated under reduced pressure up to the volume of 10–15 ml. After addition of the tenfold excess of dry ether 1.1 g (66%) of $[C_6H_6RuC_5H_5]BF_4$ in the form of white crystals without m.p. were obtained from this residue. Analytical sample was obtained by recrystallization from abs. ethanol. Found: C, 39.72; H, 3.35. $C_{11}H_{11}RuBF_4$ calcd.: C 39.89; H, 3.30%. The IR spectrum revealed the plateau typical for BF_4^- at 1020–1120 cm^{-1}.

Synthesis of $[C_6H_6RuC_5H_5]BF_4$ is described herein as a general procedure for preparation of all the other salts obtained in the present paper under high pressure.

Quantitative ratios of the reagents and reaction conditions are given in Table 1.

Preparation of anisole-cyclopentadienylruthenium tetrafluoroborate. A mixture of ruthenocene (1.15 g, 5 mmol), $AlCl_3$ (2 g, 15 mmol), Al powder (0.3 g, 10 mmol), anisole (5.5 ml, 50 mmol), containing 5 drops of water, was stirred in 50 ml of nonane in argon atmosphere at 115–125°C for 6 h. Then the reaction mixture was decomposed with ice (25 g) at 0°C and treated as described in the previous experiment. Thus was obtained 0.02 g (1.1%) of $[CH_3OC_6H_5RuC_5H_5]BF_4$, m.p. 126–132°C, (Lit. [10]: m.p. 131–134°C). The substance produces one yellow spot on the plate with Al_2O_3 (eluent was dichloroethane/ethanol, 25/4). The IR spectrum was identical to that of $[CH_3OC_6H_5RuC_5H_5]BF_4$ obtained by exchange of chlorine in $[ClC_6H_5RuC_5H_5]BF_4$ for CH_3O group [6]. The spectrum contains the frequencies 1040–1080 cm^{-1} (BF_4^-) and 1260 cm^{-1} (C_{Ar}–O).

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