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REACTIVITY OF ARENECYCLOPENTADIENYLRUTHENIUM CATIONS

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Summary

The reactivity of [AreneRuCp]$^+$ has been studied. It coincides in general with the reactivity of [AreneFeCp]$^+$. The halogens (Cl, F) in the arene ligand of [HalC$_6$H$_5$RuCp]$^+$ can be substituted smoothly by certain nucleophilic groups (PhS, HO, CN, CH$_3$O, C$_5$H$_{10}$N). The [AreneRuCp]$^+$ cations are capable of undergoing nucleophilic addition at the arene ligand by the action of NaBH$_4$ or C$_6$H$_5$Li. As a result, unsubstituted and substituted cyclohexadienylcyclopentadienylruthenium complexes are formed (C$_6$H$_7$RuC$_5$H$_5$ and *exo*-C$_6$H$_5$C$_6$H$_6$RuC$_5$H$_5$, respectively). The [CH$_3$C$_6$H$_5$RuC$_5$H$_5$]$^+$ and [C$_6$H$_5$SC$_6$H$_5$RuC$_5$H$_5$]$^+$ cations are transformed to [HOOCC$_6$H$_5$RuC$_5$H$_5$]$^+$ and [C$_6$H$_5$SO$_2$C$_6$H$_5$RuC$_5$H$_5$]$^+$ by the action of KMnO$_4$. The central ruthenium atom remains intact under these conditions. [AreneRuCp]$^+$ cations fail to reduce to AreneRuCp under the reaction conditions used for the synthesis of AreneFeCp.

Earlier we described [1] chlorine substitution in [ClC$_6$H$_5$RuC$_5$H$_5$]BF$_4$ by methoxy-, amino- and piperidino-groups. It was the first approach to study the reactivity of cationic arenecyclopentadienylruthenium derivatives. In the present paper we report new results of this investigation.

$$[\mathrm{HalC_6H_5RuC_5H_5}]\mathrm{BF_4} + \mathrm{MX} \xrightarrow{\mathrm{NaY}} [\mathrm{XC_6H_5RuC_5H_5}]\mathrm{Y} + \mathrm{MHal}$$

Hal = Cl, MX = NaOH, PhSNa (Y = PF$_6$); NaCN (Y = BPh$_4$)

Hal = F; MX = CH$_3$OH/Na$_2$CO$_3$; C$_5$H$_{10}$NH (Y = BF$_4$)

Phenol-, diphenylsulfide- and cyanobenzenecyclopentadienylruthenium cations were obtained by the substitution of chlorine in chlorobenzenecyclopentadienylruthenium tetrafluoroborate with yields of 57.5, 72 and 76%, respectively.

A high mobility exhibits the fluorine atom in [FC$_6$H$_5$RuC$_5$H$_5$]BF$_4$ *. The reac-

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* This ruthenium complex was obtained in the reaction of fluorobenzene with ruthenocene in the presence of AlCl$_3$. The synthesis and properties of this compound will be described in detail elsewhere.

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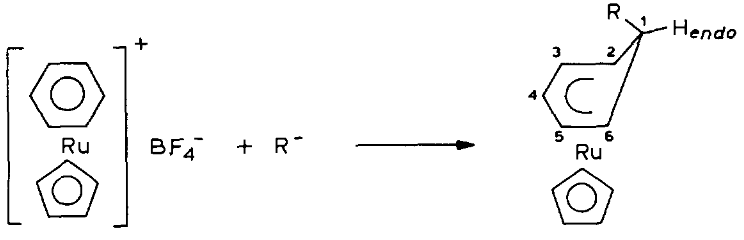
tions of this complex with methanol in the presence of Na_2CO_3, and with piperidine gave rise to $[MeOC_6H_5RuC_5H_5]BF_4$ (~100%) and $[C_5H_{10}NC_6H_5RuC_5H_5]BF_4$ (50%), respectively, obtained earlier from $[ClC_6H_5RuC_5H_5]BF_4$ [1]. In accordance with qualitative observations, the mobility of fluorine atom in $[AreneRuCp]^+$ (Cp = cyclopentadienyl) is higher than that of a chlorine atom.

All the reactions described take place under mild conditions. The high yields obtained make these reactions useful for synthetic purposes. The latter circumstance is significant, because some arenes do not exchange the ligands at ruthenocene (or ferrocene). For example, $[HOC_6H_5MC_5H_5]BF_4$ (M = Ru, Fe) was not obtained from Cp_2Ru or Cp_2Fe [2].

The degree of halide substitution in all the reactions was controlled by means of TLC on Al_2O_3. In compliance with TLC data, the substitution reactions were always quantitative. On the other hand, the fact that the yields of the substitution products were not quantitative should be explained by the difficult isolation of the reaction products and by some product decomposition during the reactions.

The results discussed above confirm that the halides in the arene ligand of $[AreneRuCp]^+$, as well as the halides in the ligand of $[AreneFeCp]^+$ [3,4], are significantly activated in comparison with the Cl and F atoms in ClC_6H_5 and FC_6H_5, respectively. Such an activation may be considered the result of delocalization of the positive charge of the $[HalC_6H_5RuC_5H_5]^+$ cations on the ligands.

Arenecyclopentadienylruthenium cations are capable of reacting with nucleophilic agents in two ways, like their iron analogues. Besides nucleophilic substitution of halogen atoms, $[AreneRuCp]^+$ cations are capable of undergoing nucleophilic addition.



R = H ($NaBH_4$) ; C_6H_5 (C_6H_5Li)

For instance, hydride ion adds to the arene ligand in benzenecyclopentadienylruthenium tetrafluoroborate in reaction with $NaBF_4$ to give light yellow cyclohexadienylcyclopentadienylruthenium in a 55% yield *. Such an addition is characteristic of all cationic arene π-complexes. In the course of this reaction, the arene ligand transforms into a non-planar cyclohexadienyl ligand.

The ^1H NMR spectrum of cyclohexadienylcyclopentadienylruthenium contains a singlet due to the cyclopentadienyl protons at δ 4.62 (5H) and a set of signals characteristic of the cyclohexadienyl ligand: δ 5.71 (t, 1H, H(4)), 4.36 (t, 2H, H(3,5)), 2.75 (m, 1H, H(*endo*)), 2.55 ppm (m, 3H, H(2,6) and H(*exo*)). The IR spectrum of

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* This reaction has been briefly described earlier [5,6].

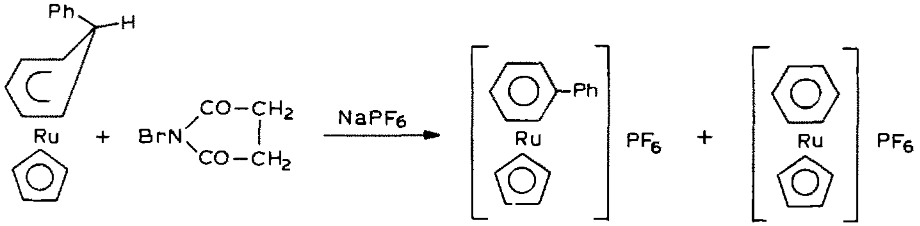
the same compound shows a band at 2780 cm^{-1}, which is characteristic of the *exo*-C–H bond of the cyclohexadienyl ligand [7].

Interaction of $[C_6H_6RuC_5H_5]BF_4$ with phenyllithium led to the formation of light yellow *exo*-phenylcyclohexadienylcyclopentadienylruthenium in an 83% yield. The ^1H NMR spectrum of this compound shows signals characteristic of cyclohexadienyl and cyclopentadienyl ligands with a substituent at the sp^3-hybridized carbon atom of the former: δ 4.71 (s, 5H, Cp), 5.56 (t, 1H, H(4)), 4.44 (t, 2H, H(3,5)), 3.44 (q, 1H, H(*endo*)), 3.07 (t, 2H, H(2,6)) 7.11–6.67 ppm (m, 5 H, Ph uncoordinated).

The *exo*-configuration of the phenyl substituent follows from the absence of the signal near 2800 cm^{-1}, characteristic of the *exo*-C–H bond in the IR spectrum of $C_6H_5C_6H_6RuC_5H_5$.

Thus, the nucleophilic addition to the benzenecyclopentadienylruthenium cation occurs in the same way as was found for the iron analogues: R^- adds to the arene ligand to occupy the *exo*-position in relation to the central metal atom.

The most characteristic reaction of the cyclohexadienyl derivatives of transition metals is the elimination of hydride ion to give cationic arene derivatives of ruthenium. Cyclohexadienylcyclopentadienylruthenium reacts with *N*-bromosuccinimide to give benzenecyclopentadienylruthenium cation. The analogous reaction of *exo*-phenylcyclohexadienylcyclopentadienylruthenium is more complex.



In this reaction a mixture of substituted and non-substituted cations of arenecyclopentadienylruthenium is formed, with the former being predominant. This result indicates that in this reaction the *exo*-Ph–C(1) bond as well as the *endo*-H–C(1) bond can be broken. The same results were found for iron analogues [8].

Earlier [9] we showed that the central metal atom of the $[AreneFeCp]^+$ cations is inert in reactions with oxidizing reagents. The same properties were found for the ruthenium π-complexes. For example, the $[AreneRuCp]^+$ cations do not transform into the doubly-charged $[AreneRuCp]^{2+}$ cations under the action of $KMnO_4$. Instead, appropriate ligand substituents are oxidized. For example, the toluenecyclopentadienylruthenium cation forms the carboxybenzenecyclopentadienylruthenium cation in reaction with potassium permanganate (80%).

$$[CH_3C_6H_5RuC_5H_5]BF_4 \xrightarrow[NH_4PF_6]{KMnO_4} [HOOCC_6H_5RuC_5H_5]PF_6$$

$$[C_6H_5SC_6H_5RuC_5H_5]PF_6 \xrightarrow{KMnO_4} [C_6H_5SO_2C_6H_5Ruc_5H_5]PF_6$$

Diphenylsulfidecyclopentadienylruthenium hexafluorophosphate gives the appropriate sulfone (81%) in reaction with $KMnO_4$.

It is known that arenes with electron-withdrawing substituents do not practically enter into exchange reactions with ferrocene [10]. The same reaction for the more passive ruthenocene is even less probable [11]. Because of this, the above-mentioned oxidation reactions are of certain synthetic value. These reactions allow us to obtain otherwise unavailable $[\text{AreneRuCp}]^+$ cations with electron-withdrawing substituents in the arene ligands.

The results obtained permit us to conclude that the reactivity of arenecyclopentadienylruthenium cations coincides for the most part with that of arenecyclopentadienyliron cations. On the other hand, non-essential quantitative differences in the properties of these cations must be revealed in special research.

A substantial difference between the properties of ruthenium and iron derivatives was discovered only by attempts to reduce $[C_6H_6RuC_5H_5]BF_4$. It is known [12] that arenecyclopentadienyliron cations reduce easily in reaction with sodium amalgam to form electroneutral AreneFeCp. Cationic derivatives of iron were studied polarographically, and it was found that the transformation $[\text{AreneFeCp}]^+ \rightarrow \text{AreneFeCp}$ occurs at $E_{1/2} = 1.07-1.55$ according to the properties of the ligands [13].

We failed to obtain AreneRuCp under the reaction conditions used for the synthesis of AreneFeCp.

$$[C_6H_6RuC_5H_5]^+ + Na/Hg \nrightarrow C_6H_6RuC_5H_5$$

Interaction of $[C_6H_6RuC_5H_5]^+$ with Na/Hg in THF takes place very actively with significant decomposition.

Cyclohexadienylcyclopentadienylruthenium was the only product detected. It was formed in an insignificant yield and its formation was proved by means of IR (presence of a band at 2780 cm^{-1}) and mass spectra. The formation of the cyclohexadienylcyclopentadienyl derivative can be considered indirect proof that the reduction of the cation still occurred. If the $C_6H_6RuC_5H_5$ formed is very reactive, it will be able to react with the solvent with abstraction of $H^\cdot$ to give cyclohexadienylcyclopentadienylruthenium. Similar processes are known for AreneFeCp [14].

On the other hand, interaction of $[C_6H_6RuC_5H_5]BF_4$ with Na/Hg in a two-phase system (pentane/water) also gave rise only to the product cyclohexadienylcyclopentadienylruthenium. It has been reported that reduction of $[\text{AreneFeCp}]^+$ to $[\text{AreneFeCp}]^-$ can take place under the same conditions. This means that the initial cation acquired two electrons. The anion formed reacted very actively with a proton to form the same cyclohexadienylcyclopentadienyl derivatives [15]. However, the mechanism of formation of $C_6H_7RuC_5H_5$ is now unclear.

It is evident that the reduction of ruthenium cations is more complex than that of iron derivatives, and this reaction has to be studied further.

It is interesting to note that a polarographic study of $[\text{AreneRuCp}]^+$ was unsuccessful [6].

Experimental

All the reactions described were carried out in an inert atmosphere. All the solvents were dried thoroughly before use. TLC control of the reactions was performed using Al_2O_3 and the solvent system dichloroethane/ethanol (25/4).

The ^1H NMR spectra were recorded with Hitachi-Perkin-Elmer R-12 (60 MHz), Bruker-SXP-4-100 and Tesla BR 467A instruments in hexadeuterioacetone with TMS as the internal standard. The IR spectra (KBr pellets) were recorded on a

UR-20 spectrometer. The mass spectra of the compounds synthesized were taken on an AEI MS-30 mass spectrometer equipped with a DS-50 data processing system. The conditions were: inlet temperature, 30°C; temperature of ionization chamber, 150°C; ionizing voltage, 70 V.

Interaction of chlorobenzenecyclopentadienylruthenium tetrafluoroborate with C_6H_5SNa

A solution of $[ClC_6H_5RuC_5H_5]BF_4$ (0.18 g, 0.5 mmol) in acetone (8 ml) was added to a solution of PhSNa (prepared from 0.15 g NaOH and 0.35 ml PhSH) in 15 ml of acetone. The mixture was kept at 20°C for 24 h. The resulting precipitate was filtered off and washed thoroughly with acetone. To the mother liquor combined with the acetone washings was added an excess of $NaPF_6$ in acetone. The mixture was concentrated to ca. 10 ml and dry ether was added. The solid that precipitated was filtered off and extracted with hot dichloroethane. White, crystalline $[C_6H_5SC_6H_5RuC_5H_5]PF_6$ (0.19 g, 72%) was isolated from the extract, m.p. 122.5–123°C (dec.), after two repeated precipitations with ether from dichloroethane solution. Found: C, 41.75; H, 3.18; Ru, 20.69; S, 6.47. $C_{17}H_{15}F_6PRuS$ calcd.: C, 41.45; H, 3.04; Ru, 20.32; S, 6.46%. ^1H NMR spectrum: δ 5.60 (s, 5H, Cp), 6.35 (s, 5H, C_6H_5 coordinated), 7.67 ppm (s, 5H, C_6H_5 uncoordinated).

The IR spectrum of the product revealed a signal in the region 840–860 cm^{-1} (PF_6^-) and signals at 1090 and 1020 cm^{-1} (unsubstituted Cp-ring).

The use of ethanol as the solvent in this reaction leads to displacement of chlorine by the C_2H_5O group.

Interaction of chlorobenzenecyclopentadienylruthenium tetrafluoroborate with NaCN

A mixture of $[ClC_6H_5RuC_5H_5]BF_4$ (0.23 g, 0.64 mmol) and NaCN (0.2 g, 4 mmol) in 15 ml of dry dimethylformamide was stirred for 4 h at 65–75°C. Then the mixture was cooled, diluted with 50 ml of water and filtered. An excess of $NaBPh_4$ in water was added to the filtrate, the solid that precipitated was filtered off and washed with water (3 × 15 ml), ethanol (2 × 10 ml), and dry ether. Then the precipitate was extracted with nitromethane and the solution treated with ether to give slightly yellow crystals of $[NCC_6H_5RuC_5H_5]BPh_4$ (0.29 g, 76%), m.p. 211–212°C (dec.), after repeated precipitation with ether from nitromethane. Found: C, 73.12; H, 5.21, N, 2.90. $C_{36}H_{30}BNRu$ calcd.: C, 73.47; H, 5.13; N, 2.90%.

In addition, $[NCC_6H_5RuC_5H_5]PF_6$ was obtained; IR spectrum: 3100–3120s, 2260w, 1340m, 1310m, 1010w, 920m, 830–860s, 780 and 765w, 560s, 435m cm^{-1}.

Interaction of chlorobenzenecyclopentadienylruthenium tetrafluoroborate with NaOH

To a solution of NaOH (0.6 g, 15 mmol) in 10 ml of water was added a solution of $[ClC_6H_5RuC_5H_5]BF_4$ (0.36 g, 1 mmol) in 10 ml of acetone. The mixture was stirred in argon atmosphere for 30 min at 20°C and kept at this temperature for 7 days. TLC showed that $[ClC_6H_5RuC_5H_5]BF_4$ was absent in the reaction mixture. Then the mixture was filtered, and acetone and some of the water were evaporated in vacuo. The residue was acidified with conc. HCl and treated with $NaPF_6$ in water. The solid that precipitated was extracted with dichloroethane. To the dichloroethane extract was added absolute ether to give $[HOC_6H_5RuC_5H_5]PF_6$ (0.23 g, 56.5%), m.p. 144–145°C (dec.), after two repeated precipitations with absolute ether from dichloroethane solution.

The IR spectrum of the sample obtained contained bands in the region 830–860

cm^{-1} (PF_6^-) and at 3120 cm^{-1} (br, OH) (compare with that reported in ref. 16). However, the ^1H NMR spectral data (δ 4.53 (s, 5H), 5.33 (s, 5H), 5.91–6.38 ppm (m, 5H) and the elemental analysis indicate conclusively that the sample of $[HOC_6H_5RuC_5H_5]PF_6$ obtained in the present work contained an unseparable admixture.

Interaction of fluorobenzenecyclopentadienylruthenium tetrafluoroborate with methanol in the presence of sodium carbonate

A mixture of $[FC_6H_5RuC_5H_5]BF_4$ (0.11 g, 0.3 mmol), Na_2CO_3 (0.3 g, 3 mmol) and 8 ml of dry methanol was boiled for 5 h. Then the mixture was cooled, a precipitate was filtered off and washed several times with acetone. The combined organic solution was evaporated to dryness, and the residue was extracted thoroughly with dichloroethane. White, crystalline $[CH_3OC_6H_5RuC_5H_5]BF_4$, m.p. 133–134.5°C (after repeated precipitation with ether from dichloroethane), was isolated from the dichloroethane extract. Found: Ru, 28.00. $C_{12}H_{13}BF_4ORu$ calcd.: Ru, 27.99%.

The IR spectrum of the sample obtained was identical to that of the sample of $[CH_3OC_6H_5RuC_5H_5]BF_4$ described earlier [1].

Interaction of fluorobenzenecyclopentadienylruthenium tetrafluoroborate with piperidine

A mixture of $[FC_6H_5RuC_5H_5]BF_4$ (0.18 g, 0.5 mmol) and 2 ml of dry piperidine in 7 ml of acetone was kept at ~ 20°C for 24 h. Then the solvent was removed in vacuo, the residue was dissolved in dichloroethane and precipitated twice with dry ether. A slightly pink coloured sample of $[C_5H_{10}NC_6H_5RuC_5H_5]BF_4$ (0.1 g, 50%), m.p. 146–148°C, was obtained after two recrystallizations from absolute ethanol. Literature data [1]: m.p. 138–140°C. Found: N, 3.47. $C_{16}H_{20}BF_4NRu$ calcd.: N, 3.38%. The IR spectrum of the sample obtained was identical to that of the sample of $[C_5H_{10}NC_6H_5RuC_5H_5]BF_4$ described earlier [1].

Oxidation of toluenecyclopentadienylruthenium tetrafluoroborate

A mixture of $[CH_3C_6H_5RuC_5H_5]BF_4$ (0.34 g, 1 mmol), $KMnO_4$ (0.64 g, 4 mmol) and water (35 ml) was boiled for 22 h. To the black suspension formed was added oxalic acid gradually to discolour the mixture. The white solid that precipitated was filtered off and washed with water (2 × 5 ml). The mother liquor and water washings were combined, acidified with HCl to pH 1, and treated with a saturated solution of $NaPF_6$ in water. The solid which precipitated was filtered off and washed consecutively with water, ether, dichloroethane, and then precipitated twice with ether from acetone solution. Found: C, 33.24; H, 2.56; P, 7.15. $C_{12}H_{11}O_2F_6PRu$ calcd.: C, 33.26; H, 2.56; P, 7.18%. The IR spectrum $[HOOCC_6H_5RuC_5H_5]PF_6$ obtained contained bands in the region 830–860 cm^{-1} (PF_6^-) and 1710 cm^{-1} (CO). ^1H NMR spectrum: δ 5.65 (s, 5H, Cp), 6.62 (3H, arene), 6.92 ppm (2H, arene).

Oxidation of diphenylsulfidecyclopentadienylruthenium hexafluorophosphate by means of $KMnO_4$

To a stirred solution of $[C_6H_5SC_6H_5RuC_5H_5]PF_6$ (0.15 g, 0.3 mmol) in acetic acid (10 ml) and water (3 ml) was added gradually at 20°C finely powdered $KMnO_4$ (0.12 g, 0.75 mmol). After being heated on a water bath for 30 min at 80°C and 30 min at 50°C, the mixture was treated with oxalic acid until the solution became colourless. The solid that precipitated was removed by filtration, washed with water (2 ml) and several portions of acetone (total volume ca. 15 ml). The combined filtrates (acetic acid, water and acetone) were concentrated in vacuo to ca. 5 ml. White, crystalline $[C_6H_5SO_2C_6H_5RuC_5H_5]PF_6$ (0.13 g, 81%) was precipitated from this residue with ether. The compound melted at 176–177°C (dec.) after two repeated precipitations with ether from dichloroethane. Found: C, 38.92; H, 2.98; S, 6.49%. $C_{17}H_{15}F_6O_2PRuS$ calcd.: C, 38.56; H, 2.85; S, 6.06%. The IR spectrum of the substance obtained contained absorbances in the region 830–860 cm^{-1} (PF_6^-) and at 1170, 1340 cm^{-1} (S=O).

Interaction of benzenecyclopentadienylruthenium tetrafluoroborate with $NaBF_4$

$NaBH_4$ (0.15 g, 4 mmol) was added in small portions at ~ 20°C to a stirred mixture of $[C_6H_6RuC_5H_5]BF_4$ (0.5 g, 1.5 mmol) and THF (25 ml). Then ~ 1 ml of water was added and the mixture was stirred for 30 min. Pentane (30 ml) was added to the resulting yellow solution, the solid that precipitated was filtered off, and the layers were separated. The organic solution was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was recrystallized from pentane on cooling with solid CO_2. The light yellow, crystalline cyclohexadienylcyclopentadienylruthenium (0.2 g, 55%) obtained melted at 117–120°C. Found: C, 53.98; H, 4.93. $C_{11}H_{12}Ru$ calcd.: C, 53.85; H, 4.93%. IR spectrum: 3020m, 2960w, 2780s, 1480w, 1440w, 1410w, 1390w, 1290s, 1100s, 1040m, 1000s, 800s, 785s cm^{-1}. Mass spectrum (m/z): 245 $[C_6H_7RuC_5H_5]^+$, 232 $[C_5H_5RuC_5H_5]^+$, 166 $[C_5H_5Ru]^+$, 78 $[C_6H_6]^+$, 77 $[C_6H_5]^+$, 66 $[C_5H_6]^+$, 65 $[C_5H_5]^+$.

Interaction of benzenecyclopentadienylruthenium tetrafluoroborate with phenyllithium

$[C_6H_6RuC_5H_5]BF_4$ (0.5 g, 1.5 mmol) was added to a stirred solution of C_6H_5Li (0.5 g, 6 mmol) in ether at −5°C. The mixture was kept at this temperature for 3 h and then allowed to warm to room temperature. Then the reaction mixture was treated with water (20 ml) and filtered. The solid obtained was dissolved in CCl_4, the solution was combined with the organic layer of the mother liquor, dried with $MgSO_4$ and evaporated to dryness in vacuo to give light yellow crystals of *exo*-phenylcyclohexadienylcyclopentadienylruthenium (0.4 g, 83%), m.p. 153–155°C after recrystallization from pentane. Found: C, 62.85: H, 4.91. $C_{17}H_{16}Ru$ calcd:: C, 63.53; H, 5.00%. IR spectrum: 3015w, 2900w, 1600w, 1490m, 1450w, 1410w, 1250w, 1100s, 1000s, 800s, 780m, 740m, 700s cm^{-1}. Mass spectrum (m/z): 321 $[C_6H_5C_6H_6RuC_5H_5]^+$, 256 $[C_6H_5C_6H_6Ru]^+$.

Interaction of cyclohexadienylcyclopentadienylruthenium with N-bromosuccinimide

To a solution of $C_6H_7RuC_5H_5$ (0.16 g, 0.7 mmol) in 10 ml of pentane at ~ 20°C in argon atmosphere was added $NaPF_6$ (0.15 g, 0.8 mmol) in methanol (15 ml) and *N*-bromosuccinimide (0.21 g, 1.6 mmol). The reaction mixture gradually turned orange and a white solid precipitated. After 30 min the solution was evaporated in vacuo, and the residue washed with water and taken up with dichloroethane. The dichloroethane extract was dried over $MgSO_4$, the solvent was evaporated, and the residue was precipitated twice with ether from dichloroethane solution to give $[C_6H_6RuC_5H_5]PF_6$ (0.14 g, 57%). The ^1H NMR spectrum of this compound was identical to that of the sample prepared by another method [7].

Interaction of exo-phenylcyclohexadienylcyclopentadienylruthenium with N-bromosuccinimide

$NaPF_6$ (0.2 g, 1 mmol) in methanol (15 ml) and *N*-bromosuccinimide (0.3 g, 2 mmol) were added to a solution of *exo*-$C_6H_5C_6H_6RuC_5H_5$ (0.3 g, 1 mmol) in benzene (10 ml) and pentane (20 ml). The procedure was the same as that above. Thus 0.25 g of a brown solid was obtained, which, as can be seen by TLC on alumina, consisted of hexafluorophosphates of two cations, $[C_6H_6RuC_5H_5]PF_6$ and $[C_6H_5C_6H_5RuC_5H_5]PF_6$, with the latter being predominant. The structures of the compounds obtained were confirmed by ^{1}H NMR data: δ 5.53 (s, 5H, Cp) and 5.56 (s, 5H, Cp), 6.44–6.95 (m, 5H, C_6H_5 coordinated) 7.42–8.0 (m, 5H, C_6H_5 uncoordinated), 6.37 ppm, (s, 6H, C_6H_6 coordinated).

Reduction of benzenecyclopentadienylruthenium tetrafluoroborate with sodium amalgam

(a) In tetrahydrofuran solution. $[C_6H_6RuC_5H_5]BF_4$ (0.4 g, 1.2 mmol) was added to 1% Na/Hg (prepared from 4 g-atoms of Na) in THF (15 ml) at −20°C. The reaction mixture was stirred for 2 h at this temperature, then the temperature was elevated to −10°C and the mixture turned brown. After 10 min the reaction mixture was cooled to −60°C, filtered in argon atmosphere into a flask with a solution of $NaBF_4$ in water (5 ml) and benzene (5 ml). Air was bubbled through this two-phase mixture, then the layers were separated. The water solution contained no π-complex products.

The organic solution was dried over $MgSO_4$ and evaporated to dryness in vacuo. The IR spectrum of the residue contained a band at 2800 cm^{-1}. Mass spectrum (m/z): 245 $[C_6H_7RuC_5H_5]^+$, 232 $[(C_5H_5)_2Ru]^+$, 166 $[RuC_5H_5]^+$, 78 $[C_6H_6]^+$, 65 $[C_5H_5]^+$.

(b) In pentane/water mixture. A solution of $[C_6H_6RuC_5H_5]BF_4$ (0.5 g, 1.5 mmol) in water (5 ml) was gradually added at −12°C to stirred 1% Na/Hg (prepared from 4 g-atoms of Na) in pentane (50 ml). The pentane layer turned red-brown. The mixture was cooled to −40°C and stirred at this temperature for 1 h. Then the pentane solution was filtered in argon atmosphere into a flask with 5 ml of a solution of $NaBF_4$ in water and treated with atmospheric oxygen as described before. The layers were separated, the organic layer was dried over $MgSO_4$ and evaporated to dryness in vacuo to give 0.05 g of light yellow crystals. The IR spectrum of the compound obtained contained a band at 2800 cm^{-1}.

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