*Journal of Organometallic Chemistry*, 246 (1983) 279–285
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# A NEW PREPARATIVE ROUTE TO CATIONIC ARENE COMPLEXES OF RUTHENIUM(II), RHODIUM(III) AND IRIDIUM(III)

M.I. RYBINSKAYA*, A.R. KUDINOV and V.S. KAGANOVICH

*A.N. Nesmeyanov Institute of Organo-Element Compounds of the Academy of Sciences of the U.S.S.R., Vavilov St. 28, Moscow 117334 (U.S.S.R.)*

(Received November 17th, 1982)

## Summary

The cationic arene complexes $[Ru(\eta\text{-arene})(\eta\text{-arene}')]Y_2$ and $[M(\eta\text{-}C_5Me_5)(\eta\text{-arene})]Y_2$ (M = Rh, Ir; Y = $BF_4$, $PF_6$) were prepared by direct exchange of chloride ligands in dimers $[Ru(\eta\text{-arene})Cl_2]_2$ and $[M(\eta\text{-}C_5Me_5)Cl_2]_2$ for arenes by refluxing in trifluoroacetic acid. The triple chloride-bridged complexes $[Ru_2(\eta\text{-arene})_2Cl_3]Y$ and $[M_2(\eta\text{-}C_5Me_5)_2Cl_3]Y$ were obtained by reaction of these dimers with acids.

## Introduction

Arene complexes of transition metals have been attracting attention of chemists for a long time. Cationic arene complexes have special interest because of their high reactivity towards nucleophiles [1]. We now report a new convenient, high-yield route to cationic arene complexes of ruthenium(II), rhodium(III) and iridium(III), based on exchange of chloride ligands in the dimers $[Ru(\eta\text{-arene})Cl_2]_2$ (I) and $[M(\eta\text{-}C_5Me_5)Cl_2]_2$ (IIa, M = Rh; IIb, M = Ir).

## Results and discussion

Until now only two methods were known for the synthesis of cationic arene complexes of ruthenium(II). The Fischer-Hafner method [2–5] gives rise to symmetrical bisareneruthenium cations $[Ru(\eta\text{-arene})_2]^{2+}$. The unsymmetrical cations $[Ru(\eta\text{-arene})(\eta\text{-arene}')]^{2+}$ have been obtained by treatment of I with silver salts in acetone [6] or water [7] followed by exchange of solvent molecules for arene in the intermediate complexes in the presence of acid ($CF_3COOH$, $HBF_4$ or $HPF_6$) or without acid (but in lower yields). $\eta$-Arene-$\eta$-pentamethylcyclopentadienylrhodium(III) and -iridium(III) complexes have been prepared similarly from IIa, b [8,9]. Taking into account that in both methods an acid ($AlCl_3$ or a strong protonic acid) is used as a catalyst, we attempted to prepare the corresponding cationic arene complexes of Ru, Rh and Ir from I and IIa, b without using silver salts by direct refluxing with arene in $CF_3COOH$. Our attempt was successful, and thus the cations

0022-328X/83/$03.00 

$[Ru(\eta\text{-arene})(\eta\text{-arene}')]^{2+}$ and $[M(\eta\text{-}C_5Me_5)(\eta\text{-arene})]^{2+}$ (M = Rh, Ir) were obtained in high yields by a one-step reaction:

$$[Ru(\eta\text{-arene})Cl_2]_2 \xrightarrow[CF_3COOH]{\text{arene}'} [Ru(\eta\text{-arene})(\eta\text{-arene}')]^{2+}$$

$$[M(\eta\text{-}C_5Me_5)Cl_2]_2 \xrightarrow[CF_3COOH]{\text{arene}} [M(\eta\text{-}C_5Me_5)(\eta\text{-arene})]^{2+}$$

M = Rh, Ir

The cations were isolated in the form of hexafluorophosphate and tetrafluoroborate salts.

It is interesting to note that the use of $AlCl_3$ in this reaction instead of a strong protonic acid ($CF_3COOH$) also proved to be efficient, but $AlCl_3$ catalysis must be carried out under an inert atmosphere and can be used with success only for arenes without functional groups. Carrying out these reactions in trifluoroacetic acid takes away the limitations of using arenes with some functional groups and does not require an inert atmosphere. As it was shown for the example of bisareneruthenium cations, complexes containing arenes with functional groups can be obtained by this method (see Table 1). This reaction turned out to occur only in a strong protonic acid such as $CF_3COOH$. The reaction is considerably accelerated by addition of $(CF_3CO)_2O$ to the reaction mixture. Acetic acid cannot be used for this reaction, but the use of a $HBF_4$-$CH_3COOH$ mixture gives positive results.

We did not investigate the mechanism of this reaction in detail, but we studied the behaviour of the initial complex $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ in trifluoroacetic acid. This complex is known to be practically insoluble in most organic solvents (except DMSO), but turned out to be readily soluble in $CF_3COOH$ at ambient temperature. This solution shows $\delta$ 5.41 ppm (s) in its $^1H$ NMR spectrum, the same signal was observed for $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ in $CF_3COOH$. When the acid was evaporated off and the residue was treated with aqueous $NH_4PF_6$, the complex $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]PF_6$ was obtained. The corresponding tetrafluoroborate salt was also isolated. By heating the complex $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ with mesitylene in $CF_3COOH$ the cationic bisarene complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-mes})](BF_4)_2$ was obtained in quantitative yield. When refluxed in $CF_3COOH$ in the absence of arene, the cation $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ remains unchanged. Thus, the interaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with arene in trifluoroacetic acid can be supposed to occur via initial formation of the triple chloride-bridged cation $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$, which reacts further with direct exchange of chloride ligands for arene, or via intermediate exchange of chloride ligands for trifluoroacetic anions followed by their exchange for arene:

$$[Ru(\eta\text{-}C_6H_6)Cl_2]_2 \xrightarrow{CF_3COOH} [Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+ \xrightarrow[CF_3COOH]{\text{arene}} [Ru(\eta\text{-}C_6H_6)(\eta\text{-arene})]^{2+}$$

Preparation of the triple chloride-bridged complexes of type $[Ru_2(\eta\text{-arene})_2Cl_3]^+$ is of independent interest. Some methods have been described for their synthesis [10–13], but only the complex with benzene has been prepared in a high yield by one-step reaction of I with $NH_4PF_6$ in methanol [11]. We tried to prepare triple chloride-bridged areneruthenium complexes by interaction of I with various acids.

TABLE 1

REACTION TIMES, YIELDS AND ANALYTICAL DATA FOR COMPLEXES [Ru($\eta$-arene)($\eta$-arene')]$Y_2$

| Arene | Arene' | Y | Time (h) | Yield (%) | Anal. (Found (calc.) (%)) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | P (or B) | F | Ru |
| $C_6H_6$ | $C_6H_5Me$ | $PF_6$ | 5 | 87 | 27.77 (27.82) | 2.50 (2.51) | 10.96 (11.04) | – | 17.91 (18.01) |
| $C_6H_6$ | 1,3,5-$C_6H_3Me_3$ | $PF_6$ | 1.5 | 88 | 30.34 (30.57) | 3.00 (3.08) | 10.27 (10.51) | – | 17.63 (17.15) |
| $C_6H_6$ | $C_6H_5NH_2$ | $PF_6$ | 10 | 89 | 26.16 (25.63) | 2.49 (2.33) | 10.93 (11.02) | – | 18.09 (17.98) |
| $C_6H_6$ | $C_6H_5OEt$ | $PF_6$ | 2 | 87 | 27.94 (28.44) | 2.78 (2.73) | 10.29 (10.48) | – | 16.95 (17.09) |
| $C_6H_6$ | $C_6H_6$ | $BF_4$ | 12(2 [a]) | 93 | 33.48 (33.45) | 2.84 (2.81) | 4.98 (5.02) | 34.49 (35.28) | – |
| $C_6H_6$ | $C_6H_5Me$ | $BF_4$ | 5 | 95 | 34.87 (35.09) | 3.47 (3.17) | 4.87 (4.86) | 34.22 (34.16) | – |
| $C_6H_6$ | 1,4-$C_6H_4Me_2$ | $BF_4$ | 3 | 96 | 36.91 (36.64) | 3.94 (3.51) | 4.77 (4.71) | 32.66 (33.12) | – |
| $C_6H_6$ | 1,3,5-$C_6H_4Me_3$ | $BF_4$ | 1.5 | 94 | 38.11 (38.09) | 4.17 (3.84) | 4.59 (4.57) | 32.16 (32.14) | – |
| $C_6H_6$ | $C_6Me_6$ | $BF_4$ | 6(1 [a]) | 97 | 41.52 (41.97) | 4.57 (4.70) | 4.04 (4.20) | 29.37 (29.51) | – |
| $C_6H_6$ | 1,3,5-$Me_3C_6H_2(CH_2)_3COOH$ [b] | $BF_4$ | 1.5 | 89 | 40.69 (40.82) | 4.10 (4.33) | – | 26.62 (27.19) | – |
| 1,3,5-$C_6H_3Me_3$ | 1,3,5-$C_6H_3Me_3$ | $BF_4$ | 1.5 | 94 | 41.69 (41.97) | 4.72 (4.70) | – | 29.88 (29.51) | – |

[a] When trifluoroacetic anhydride (1 ml) was added to the reaction mixture. [b] IR ($cm^{-1}$, KBr) 1710s [$\nu$(C=O)].

The use of $HBF_4$ proved to be the simplest preparative route:

$$[Ru(\eta\text{-arene})Cl_2]_2 \xrightarrow[S]{HBF_4} [Ru_2(\eta\text{-arene})_2Cl_3]BF_4$$

a) arene = $C_6H_6$, S = MeOH;

b) arene = mes, S = $MeOH/MeNO_2$

The isoelectronic rhodium complex $[Rh_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$ was prepared earlier by similar reaction of IIa with $HBF_4$ in $CH_2Cl_2$ [14]. We obtained this complex by treatment with 48% aqueous $HBF_4$ in MeOH, but the preparation of the corresponding iridium complex $[Ir_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$ was successful only with a solution of 48% aqueous $HBF_4$ in acetic anhydride in $CH_2Cl_2$ as a solvent. Both these complexes were also isolated after addition of $HBF_4$ to solutions of IIa, b in $CF_3COOH$. The formation of the cations $[M_2(\eta\text{-}C_5Me_5)_2Cl_3]^+$ (M = Rh, Ir) from IIa, b was shown to be a reversible reaction. When chloride ion (in the form of hydrochloric acid) was added to a solution of $[M_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$ in MeOH, crystals of the corresponding dimer IIa, b were formed.

## Experimental

IR spectra were recorded on a UR-20 spectrometer. $^1H$ NMR spectra were obtained on Perkin-Elmer R-12 and Hitachi-Perkin-Elmer R-20 (60 MHz) instruments with HMDS as internal reference. Trifluoroacetic acid was distilled before use. Preparations of the dicationic arene complexes were carried out with protection from atmospheric moisture.

*Preparation of [Ru(η-arene)(η-arene')]$Y_2$ complexes*

*(i) Y = $PF_6$*

A mixture of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.125 g, 0.25 mmol), arene (0.5 ml) and $CF_3COOH$ (3 ml) was refluxed until change of the colour from orange-brown to yellowish. The solution was evaporated in vacuo and the residue was dissolved in water (~ 3 ml). An excess of $NH_4PF_6$ was added to the filtrated aqueous solution. The precipitate was centrifuged off, dried in vacuo and reprecipitated from acetone with ether to give a white solid. The reaction times, yields and analytical data are given in Table 1.

*(ii) Y = $BF_4$*

*(a) Using $CF_3COOH$.* After refluxing a mixture of $[Ru(\eta\text{-arene})Cl_2]_2$ (0.25 mmol), arene (0.5 ml for liquid and 0.2 g for solid arenes) and $CF_3COOH$ (3 ml) until disappearance of the initial colour, 48% aqueous $HBF_4$ (~ 0.3 ml) was added, and the reaction mixture was evaporated in vacuo. The residue was reprecipitated from $MeNO_2/Et_2O$ to give a white solid. The reaction times, yields and analytical data are given in Table 1. The tetrafluoroborates (except the complex with *p*-xylene) can be also isolated by careful addition of $Et_2O$ to the filtrated reaction mixture.

*(b) Using $HBF_4$-$CH_3COOH$.* A mixture of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.125 g, 0.25 mmol), mesitylene (0.5 ml) and ~ 1.4 *N* solution of $HBF_4$ in acetic acid (5 ml; obtained from 48% aqueous $HBF_4$ and acetic anhydride) was stirred under reflux until disap-

pearance of the orange solid (~ 0.5 h). Ether (~ 10 ml) was added dropwise to the cooled reaction mixture and the precipitate was centrifuged off and reprecipitated from $MeNO_2/Et_2O$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-mes})](BF_4)_2$ (0.228 g, 96%). The complex was identified by elemental analysis and its $^1H$ NMR spectrum in DMSO-$d_6$ (three singlets at $\delta$ 2.46, 7.11 and 7.16 ppm in the intensity ratio 3 : 2 : 1, cf. [6]).

*Preparation of $[Rh(\eta\text{-}C_5Me_5)(\eta\text{-arene})]Y_2$ complexes ($Y = PF_6$, $BF_4$)*

*(a) Using $CF_3COOH$.* A mixture of $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.155 g, 0.25 mmol), arene (0.5 ml, for $C_6Me_6$: 0.2 g) and $CF_3COOH$ (3 ml) was refluxed until disappearance of the initial deep red colour. Isolation of hexafluorophosphates and tetrafluoroborates (white solids) was carried out as described above for the ruthenium complexes. The reaction times, yields and analytical data are given in Table 2. The $^1H$ NMR spectrum of $[Rh(\eta\text{-}C_5Me_5)(\eta\text{-mes})](PF_6)_2$ (in acetone-$d_6$) shows three singlets at $\delta$ 2.35, 2.67 and 7.58 ppm in the intensity ratio 5 : 3 : 1 (cf. [9]).

*(b) Using $HBF_4$-$CH_3COOH$.* A mixture of $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.155 g, 0.25 mmol), mesitylene (0.5 ml) and ~ 1.4 *N* $HBF_4$/acetic acid (5 ml) was refluxed until disappearance of the initial colour (~ 10 min). Ether (~ 10 ml) was added carefully to the cooled solution and the precipitate was centrifuged off and reprecipitated from $MeNO_2/Et_2O$ to give $[Rh(\eta\text{-}C_5Me_5)(\eta\text{-mes})](BF_4)_2$ (0.245 g, 92%), which was identified by elemental analysis and IR spectrum.

*Preparation of $[Ir(\eta\text{-}C_5Me_5)(\eta\text{-arene})]Y_2$ complexes ($Y = PF_6$, $BF_4$)*

A mixture of $[Ir(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.199 g, 0.25 mmol), arene (0.5 ml, for

TABLE 2

REACTION TIMES, YIELDS AND ANALYTICAL DATA FOR COMPLEXES $[M(\eta\text{-}C_5Me_5)(\eta\text{-arene})]Y_2$ (M = Rh, Ir)

| M | Arene | Y | Time (h) | Yield (%) | Anal. (Found (calc.)(%)) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | P (or B) | F |
| Rh | 1,3,5-$C_6H_3Me_3$ | $PF_6$ | 1 | 87 | 35.14 (35.20) | 4.16 (4.19) | 9.56 (9.55) | – |
| Rh | $C_6Me_6$ | $PF_6$ | 1 | 85 | 38.21 (38.28) | 4.89 (4.82) | 8.94 (8.97) | – |
| Rh | $C_6H_6$ | $BF_4$ | 4 [a] | 91 | 38.69 (39.23) | 4.36 (4.32) | – | 31.08 (31.03) |
| Rh | 1,3,5-$C_6H_3Me_3$ | $BF_4$ | 1 | 92 | 42.73 (42.90) | 5.12 (5.12) | 4.13 (4.06) | 28.51 (28.57) |
| Rh | $C_6Me_6$ | $BF_4$ | 1 | 94 | 45.69 (46.03) | 5.76 (5.79) | 3.71 (3.77) | 25.94 (26.48) |
| Ir | $C_6H_6$ | $PF_6$ | 2.5 [a] | 96 | 27.53 (27.63) | 2.73 (3.04) | – | – |
| Ir | $C_6H_6$ | $BF_4$ | 2.5 [a] | 97 | 32.87 (33.18) | 3.43 (3.66) | – | 25.74 (26.25) |
| Ir | 1,3,5-$C_6H_3Me_3$ | $BF_4$ | 2.5 | 94 | 36.62 (36.73) | 4.05 (4.38) | – | 24.54 (24.47) |
| Ir | $C_6Me_6$ | $BF_4$ | 7 | 98 | 40.14 (39.83) | 5.07 (5.01) | – | 21.96 (22.92) |

[a] When trifluoroacetic anhydride (1 ml) was added to the reaction mixture.

$C_6Me_6$ : 0.2 g) and $CF_3COOH$ (3 ml) was refluxed until disappearance of the initial yellow colour. The hexafluorophosphates and tetrafluoroborates (white solids) were isolated as described above for the ruthenium complexes. The reaction times, yields and analytical data are given in Table 2. The $^1H$ NMR spectrum of the complex $[Ir(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)](PF_6)_2$ (in DMSO-$d_6$) contains two singlets at $\delta$ 2.25 and 7.41 ppm with intensity ratio 5 : 2 (cf. [8]).

*Preparation of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]Y$ ($Y = PF_6$, $BF_4$)*

*(i) $Y = PF_6$*

A solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.125 g, 0.25 mmol) in $CF_3COOH$ (~ 3 ml) was evaporated in vacuo and the residue was dissolved in water (~ 3 ml). An excess of $NH_4PF_6$ was added to the filtrated solution and the precipitate was centrifuged off after standing for ~ 2 h, dried in vacuo and reprecipitated from $MeNO_2/Et_2O$ to give an orange-yellow solid (0.128 g, 84%). Found: C, 23.81; H, 1.90; Cl, 17.33; P, 5.17; Ru, 33.18. $C_{12}H_{12}Cl_3F_6PRu_2$ calcd.: C, 23.64; H, 1.98; Cl, 17.44; P, 5.08; Ru, 33.15%.

*(ii) $Y = BF_4$*

48% aqueous $HBF_4$ (~ 0.3 ml) was added to a solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.125 g, 0.25 mmol) in $CF_3COOH$ (~ 3 ml) and the mixture was evaporated in vacuo. The residue was reprecipitated from $MeNO_2/Et_2O$ to give an orange-yellow solid (0.127 g, 92%). Found: C, 26.53; H, 1.98; Cl, 19.04; F, 14.02. $C_{12}H_{12}BCl_3F_4Ru_2$ calcd.: C, 26.13; H, 2.19; Cl, 19.28; F, 13.78%. $^1H$ NMR ($MeNO_2$): $\delta$ 6.06 ppm (s) (cf. [13]). $^1H$ NMR ($CF_3COOH$): $\delta$ 5.41 ppm (s).

The same complex was obtained when a mixture of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.125 g, 0.25 mmol), MeOH (5 ml) and 48% $HBF_4$ (0.5 ml) was stirred at room temperature for 1 h. The orange-yellow solid was centrifuged off and reprecipitated from $MeNO_2/Et_2O$. Yield 0.130 g (94%).

*Preparation of $[Ru_2(\eta\text{-mes})_2Cl_3]BF_4$*

48% aqueous $HBF_4$ (~ 0.3 ml) was added to a solution of $[Ru(\eta\text{-mes})Cl_2]_2$ (0.146 g, 0.25 mmol) in $CF_3COOH$ (~ 3 ml) and the resulting solution was evaporated in vacuo. The residue was reprecipitated from $MeNO_2/Et_2O$ to give an orange-yellow solid (0.138 g, 87%). Found: C, 34.03; H, 3.69; Cl, 16.04; F, 12.04. $C_{18}H_{24}BCl_3F_4Ru_2$ calcd.: C, 34.01; H, 3.81; Cl, 16.73; F, 11.96.

The same complex was obtained by stirring a mixture of $[Ru(\eta\text{-mes})Cl_2]_2$ (0.073 g, 0.125 mmol), MeOH (5 ml), $MeNO_2$ (10 ml) and 48% aqueous $HBF_4$ (1 ml) for 1 h followed by addition of $Et_2O$ (~ 80 ml) to the filtrated solution. Yield 0.045 g (57%).

*Preparation of $[Rh_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$*

A mixture of $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.078 g, 0.125 mmol), 48% $HBF_4$ (0.2 ml) and MeOH (2 ml) was heated to give a solution, which was then set aside overnight at room temperature. The rhombic orange crystals thus formed were separated and washed with MeOH (~ 1 ml) and $Et_2O$. Yield 0.070 g (84%). Found: C, 35.72; H, 4.55; Cl, 15.45; F, 11.31. $C_{20}H_{30}BCl_3F_4Rh_2$ calcd.: C, 35.88; H, 4.52; Cl, 15.89; F, 11.35%. $^1H$ NMR spectrum ($CDCl_3$): $\delta$ 1.65 ppm (s) (cf. [14]).

The same complex was prepared by addition of 48% aqueous $HBF_4$ (~ 0.3 ml) to a solution of $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.078 g, 0.125 mmol) in a small amount of $CF_3COOH$ (~ 1 ml) followed by evaporation of the resulting solution in vacuo. The residue was washed with $Et_2O$ and reprecipitated from $CHCl_3/Et_2O$ to give an orange solid (0.074 g, 89%).

*Preparation of $[Ir_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$*

48% aqueous $HBF_4$/acetic anhydride (~ 1 ml) was added to a solution of $[Ir(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.100 g, 0.125 mmol) in $CH_2Cl_2$ (~ 5 ml) and the resulting yellow solution was evaporated in vacuo. The residue was washed with $Et_2O$ and reprecipitated from $CHCl_3/Et_2O$ to give a yellow solid (0.104 g, 98%). Found: C, 28.75; H, 3.24; Cl, 12.58; F, 8.56. $C_{20}H_{30}BCl_3F_4Ir_2$ calcd.: C, 28.32; H, 3.57; Cl, 12.54; F, 8.96%. $^1H$ NMR spectrum ($CDCl_3$): $\delta$1.68 ppm (s).

The same complex was prepared by addition of 48% aqueous $HBF_4$ (~ 0.3 ml) to a solution of $[Ir(\eta\text{-}C_5Me_5)Cl_2]_2$ (0.100 g, 0.125 mmol) in a small amount of $CF_3COOH$ (~ 1 ml) followed by evaporation of the solution in vacuo and reprecipitation of the residue from $CHCl_3/Et_2O$. Yield 0.102 g (96%).

*Preparation of $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}mes)](BF_4)_2$ from $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$*

After refluxing a mixture of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ (0.138 g, 0.25 mmol), mesitylene (0.5 ml) and $CF_3COOH$ (3 ml) until disappearance of the initial colour (~ 1.5 h), 48% aqueous $HBF_4$ (~ 0.3 ml) was added and the complex was precipitated by careful addition of $Et_2O$. Yield 0.236 g (100%). The complex was identified by elemental analysis and from its IR spectrum.

*Reaction of $[M_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$ (M = Rh, Ir) with HCl*

38% hydrochloric acid (~ 0.3 ml) was added to a solution of $[M_2(\eta\text{-}C_5Me_5)_2Cl_3]BF_4$ (0.100 g) in MeOH (~ 20 ml). The orange crystals of $[Ir(\eta\text{-}C_5Me_5)Cl_2]_2$ were formed immediately, the dark red crystals of $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ only on standing overnight. Yields: 0.072 g, 76% (M = Ir); 0.050 g, 54% (M = Rh). The complexes were identified by elemental analysis and from IR and $^1H$ NMR spectra.

## References


1 W.E. Silvertorn, Adv. in Organometal. Chem., 13 (1975) 48.
2 E.O. Fischer and R. Böttcher, Z. Anorg. Allg. Chem., 291 (1957) 305.
3 D. Jones, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 4458.
4 E.O. Fischer, C. Elschenbroich and C.G. Kreiter, J. Organometal. Chem., 7 (1967) 481.
5 E.O. Fischer and C. Elschenbroich, Chem. Ber., 103 (1970) 162.
6 M.A. Bennett and T.W. Matheson, J. Organometal. Chem., 175 (1979) 87.
7 M.I. Rybinskaya, V.S. Kaganovich and A.R. Kudinov, J. Organometal. Chem., 235 (1982) 215.
8 C. White and P.M. Maitlis, J. Chem. Soc., A, (1971) 3322.
9 C. White, S.J. Thompson and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1977) 1654.
10 M.A. Bennett and A.K. Smit, J. Chem. Soc. Dalton Trans., (1974) 233.
11 D.R. Robertson, T.A. Stephenson and T. Arthur, J. Organometal. Chem., 162 (1978) 121.
12 T. Arthur and T.A. Stephenson, J. Organometal. Chem., 168 (1979) C39.
13 T. Arthur and T.A. Stephenson, J. Organometal. Chem., 208 (1981) 369.
14 W. Rigby, J.A. McCleverty and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1979) 382.