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CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM COMPLEXES

III *. CHEMICAL MECHANISM OF DISSOLUTION OF CHLORO(η-CYCLOPENTADIENYL)-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) IN POLAR SOLVENTS

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Summary

The conversion of $CpRuCl(PPh_3)_2$ in boiling ethylene glycol within 90 h of reflux has been investigated. New complex cations in the form of their tetraphenylborates, for which the formulae $[Cp^1RuCl(PPh_3)PPh_2Cp^2Ru(\eta\text{-}C_6H_5)]^+$ and $[CpRu(\eta\text{-}C_6H_5)PPh_2]^+$ are proposed, were isolated. The former cation is also formed at lower temperatures during the reflux of $CpRuCl(PPh_3)_2$ in methanol. The following process takes place: $2CpRuCl(PPh_3)_2 \rightarrow [Cp^1RuCl(PPh_3)PPh_2Cp^2Ru(\eta\text{-}C_6H_5)]^+ + Cl^- + 2PPh_3$. In the presence of dicyclopentadiene during the reflux of $CpRuCl(PPh_3)_2$ in high boiling polar solvents (ethylene glycol, dimethyl sulphoxide), ruthenocene is formed in a 90% yield. One of the cyclopentadienyl groups in ruthenocene originates from dicyclopentadiene. As a result of the reaction of $CpRuCl(PPh_3)_2$ and $NaBPh_4$ in a mixture of diglyme and methanol, a colourless, crystalline compound, $CpRu(\eta\text{-}C_6H_5)BPh_3$, is obtained in a 50–60% yield.

Introduction

Since its discovery in 1969 by Gilbert and Wilkinson [1], $CpRuCl(PPh_3)_2$ has been the source of many interesting reactions [2]. A simple synthesis method introduced by Bruce and Windsor in 1977 [3] brought about a rapid increase in the number of papers published concerning the reactivity of $CpRuCl(PPh_3)_2$. The structure of the compound was also determined by X-ray methods [2,4]. Despite considerable melting temperature differences [4], it is identical to the structure given by Bruce et al. [2].

* For Part II see Ref. 4.

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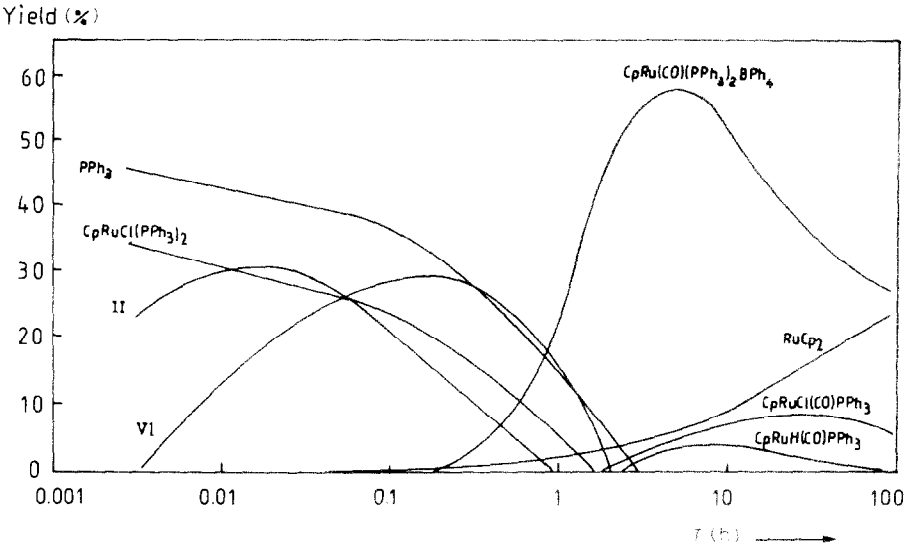


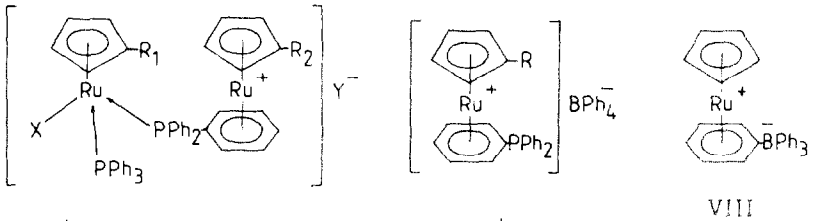
Fig. 1. $CpRuCl(PPh_3)_2$ ethylene glycol system. Yields of the compounds vs. reflux time.

Results and discussion

In Fig. 1 the yield of the compound formed in significant quantities during the reflux of $CpRuCl(PPh_3)_2$ in ethylene glycol is shown. In ethylene glycol at boiling temperature a considerable amount of $CpRuCl(PPh_3)_2$ (0.2 mol/dm^3) dissolves, forming an orange-yellow solution. In the case of short reflux times (up to 1 h), after cooling the solution some $CpRuCl(PPh_3)_2$ precipitates (up to 30–40% recovery). The remaining amount of $CpRuCl(PPh_3)_2$ in the solution exists as a complex cation, which can be isolated in the form of sparingly soluble tetraphenylborates. The dissolution process of $CpRuCl(PPh_3)_2$ is suggested to be as follows:

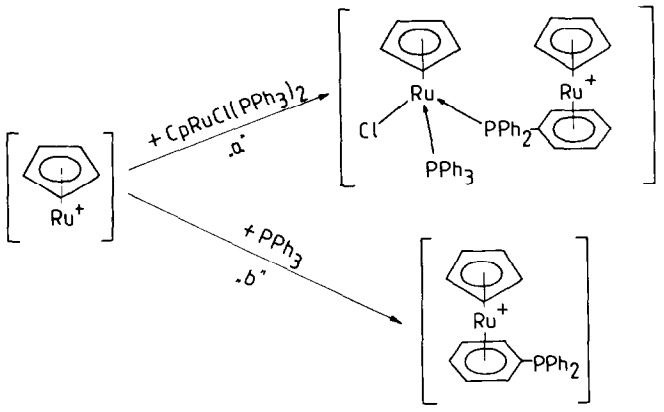
$$2\ CpRuCl(PPh_3)_2 \rightarrow Cp^1RuCl(PPh_3)PPh_2Cp^2Ru^+(\eta\text{-}C_6H_5)Cl^- + 2\ PPh_3 \qquad (1)$$

The yield of the isolated PPh_3 (beginning of the reflux, Fig. 1) confirms the above equation. This process also proceeds at lower temperatures, e.g. in methanol. In this



	X	R_1	R_2	Y
I	Cl	H	H	Cl
II	Cl	H	H	BPh_4
III	I	H	H	BPh_4
IV	Cl	Me	Me	BPh_4
V	Cl	H	Me	BPh_4

	R
VI	H
VII	Me



SCHEME 1

case, only one complex cation in the form of its tetraphenylborate (II) is isolated. As a result of the reflux of $CpRuCl(PPh_3)_2$ in high boiling ethylene glycol (197–198°C), a cation in the form of tetraphenylborate VI is also obtained.

To explain the mechanism of dissolution of $CpRuCl(PPh_3)_2$, its dissociation must be assumed:

$$CpRuCl(PPh_3)_2 \rightarrow CpRu^+ + Cl^- + 2\ PPh_3 \qquad (2)$$

with synchronous solvation of the intermediate cation $CpRu^+$ by formation of π-bonds with the nearest phenyl ring originating from a $CpRuCl(PPh_3)_2$ or PPh_3 molecule (Scheme 1).

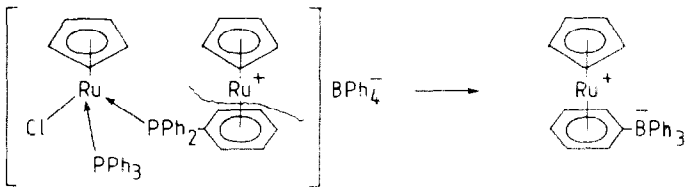
From experimental data it follows that process "a" is preferred. Rearrangement of the obtained tetraphenylborates II–VII with the formation of a solvation sphere at the ruthenium atom, consisting of a phenyl ring originating from the BPh_4^- anion, is also possible. In this way, a non-ionic compound, $CpRu(\eta\text{-}C_6H_5)BPh_3$ (VIII), has been obtained. The solution of $CpRuCl(PPh_3)_2$ in diethylene glycol dimethyl ether (diglyme) obtained during a short reflux contains $CpRuCl(PPh_3)_2$, as can be seen from the ^{31}P NMR spectrum ($\delta + 38.4$ ppm). After the addition of a solution of $NaBPh_4$ in MeOH and storage of the solution at room temperature for a few days, colourless crystals of VIII begin to precipitate. The reaction rate of the formation of VIII increases, reaching a maximum after approximately 12 days (total yield 50–60%). $CpRu(\eta\text{-}C_6H_5)BPh_3$ (VIII) was obtained earlier by Kruger et al. [5] in the form of brown crystals with a 20% yield.

In the system $CpRuCl(PPh_3)_2/NaBPh_4$/diglyme/MeOH, the process illustrated by eq. 1 probably proceeds in the following way:

$$2\ CpRuCl(PPh_3)_2 + NaBPh_4 \rightarrow II + 2\ PPh_3 + NaCl \qquad (3)$$

Due to the excellent solubility of compound II in diglyme, a non-ionic, sparingly soluble compound, $CpRu(\eta\text{-}C_6H_5)BPh_3$ (VIII), precipitates from this system as a result of the rearrangement of II (Scheme 2).

It was found that from solution II in diglyme and MeOH colourless crystals of compound VIII also precipitate after storing the solution at room temperature for several days. In the preparation of the above complexes, traces of oxygen were not rigorously excluded from the system because the presence of oxygen could shift the



II VIII

SCHEME 2

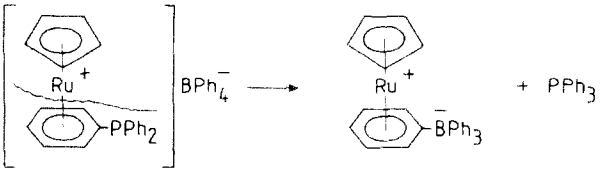
equilibrium of process (1) to the right, as a result of the formation of triphenylphosphine oxide.

The mass spectra of compounds II–V were recorded using the FD technique. They always contained the fragment $[CpRu(\eta\text{-}C_6H_5)PPh_2]^+$ (*m/e* 429) obtained from compounds II and III, or the fragment $[(\eta\text{-}C_5H_4Me)Ru(\eta\text{-}C_6H_5)PPh_2]^+$ (*m/e* 443) obtained from compounds IV and V. The ion signals at *m/e* 429 and 443 are also parent ions for compounds VI and VII, respectively. With more intensive heating of the MS device, emitter ion signals at *m/e* 262 and 486 were detected as a result of rearrangement of compound VI (Scheme 3). It is known that in all cases the MS(FD) spectra of onium salts [6] contain a complex cation signal. This has also been confirmed in the present work.

In the mass spectrum of compound VI, the fragment at *m/e* 167 corresponding to the $[CpRu]^+$ cation was not found. Only a set of signals (connected with, as previously stated, the natural abundance of ruthenium isotopes in nature) with a maximum at *m/e* 245 was found, to which the ion $[CpRu(\eta\text{-}C_6H_6)]^+$ was ascribed, obtained as a result of fragmentation of compound VI.

The above facts are evidence of negligible probability of the existence, in the solutions, of the $CpRu^+$ cation in a non-solvated state. However, the life-time of the $CpRu^+$ cation is probably sufficiently long, for instance, to allow the formation of VIII to proceed as a result of the displacement reaction of the $CpRu^+$ cation (Schemes 2 and 3).

Rearrangement of $CpRuCl(PPh_3)_2$ at the boiling temperature of ethylene glycol to a stable ruthenocene is also possible. During short reflux times (up to 1 h) the yield of ruthenocene is insignificant (2–3%, Fig. 1) and it increases with reflux time. But carrying out the reflux process in the presence of dicyclopentadiene causes



VI VIII

m/e 429 486 262

SCHEME 3

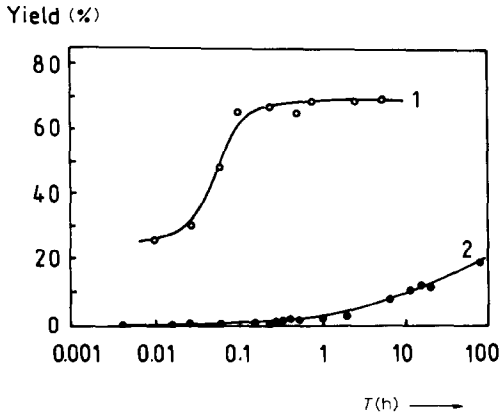


Fig. 2. Yields of ruthenocene vs. reflux time. Curve 1 $CpRuCl(PPh_3)_2$-ethylene glycol/dicyclopentadiene system (3-fold excess); curve 2 $CpRuCl(PPh_3)_2$/ethylene glycol system.

ruthenocene to be formed in a high yield (Fig. 2). At the boiling temperature of ethylene glycol, cyclopentadiene, C_5H_6 (CpH), is formed from dicyclopentadiene as a result of thermal decomposition, and it immediately reacts with $CpRu^+$ to form ruthenocene in accordance with the following equation:

$$CpRuCl(PPh_3)_2 + CpH \rightarrow RuCp_2 + PPh_3 \cdot HCl + PPh_3 \quad (4)$$

According to eq. 4, the yield of the isolated PPh_3 should be 50%. In fact this yield was observed within the time range 0.1–10 h of reflux. The simple compound $PPh_3 \cdot HCl$ was not isolated from the post-reaction mixture but more complex phosphonium salts were obtained. Excess dicyclopentadiene has a significant effect on the yield of ruthenocene (Table 1).

The highest yield of ruthenocene (90%) was obtained during a 1 h reflux of $CpRuCl(PPh_3)_2$ and dicyclopentadiene (6-fold excess) in high boiling polar solvents (ethylene glycol, dimethyl sulphoxide).

TABLE 1

$CpRuCl(PPh_3)_2$/DICYCLOPENTADIENE/ETHYLENE GLYCOL SYSTEM. REFLUX TIME 10 MIN

$n = \frac{C_{10}H_{12}}{CpRuCl(PPh_3)_2}$	Yield (%)			
	$RuCp_2$	PPh_3	$CpRuCl(PPh_3)_2$	VI
0	0	34	27	35
0.5	11	45	32	32
1.1	20	53	27	34
1.5	36	50	23	26
1.6	29	53	24	28
2.0	43	58	18	24
2.4	52	74	14	22
3.1	57	67	9	14
7.4	64	55	0	0
8.3	72	71		

To demonstrate the origin of the cyclopentadienyl groups in the prepared ruthenocene, a methyl derivative substrate, $(\eta\text{-}C_5H_4Me)RuCl(PPh_3)_2$, was used. In the presence of dicyclopentadiene it was found that methylruthenocene is formed in a yield in accordance with curve 1 (Fig. 2). 1,1'-Dimethylruthenocene was obtained in the absence of dicyclopentadiene in a yield in accordance with curve 2 (Fig. 2).

During longer reflux times (1–90 h) the cation $[CpRu(CO)(PPh_3)_2]^+$ is formed, which was isolated in the form of tetraphenylborate with a yield of up to 60%. The compound $[CpRu(CO)(PPh_3)_2]BPh_4$ has already been described by Blackmore et al. [7], who obtained it by carbonylation of $CpRuCl(PPh_3)_2$ and $NaBPh_4$ solution (52% yield). During longer times of reflux (Fig. 1), $CpRuCl(CO)PPh_3$ and $CpRuH(CO)PPh_3$ are also formed in insignificant yields.

Structures for the complex cations $[Cp^1RuCl(PPh_3)PPh_2Cp^2Ru(\eta\text{-}C_6H_5)]^+$ and $[CpRu(\eta\text{-}C_6H_5)PPh_2]^+$ have been proposed on the basis of the following data.

(i) The ^{31}P NMR spectra of compounds I and II have a set of signals (43.3, 41.5, 38.1 and 36.4 ppm) which are a doublet of doublets with coupling constants $J(P^1P^2)$ 43 Hz. The character of the spectrum is independent of the method of preparation of I and II and independent of the kind of solvent used for preparing the solution sample (methylene chloride, chloroform, pyridine, acetone).

The ^{31}P NMR (pyridine) spectrum of compound VI shows the presence of a singlet at −6.1 ppm, whose position in practice is superimposed on the position of the signal of free PPh_3 (−6.0 ppm). This indicates a lack of involvement in the bond of the electron pair on the phosphorus atom. Introduction of a methyl group to the cyclopentadienyl ring (compound VII) causes an increase of the electron density on the phosphorus atom (δ_{VII} − 7.7 ppm).

(ii) The ^1H NMR ($CDCl_3$) spectrum of compound II shows the presence of singlets at 4.0 ppm (Cp^1) and 4.3 ppm (Cp^2), two multiplets at 4.8 and 5.6 ppm, corresponding to the protons of the phenyl ring π-bonded to an atom of ruthenium, as well as signals corresponding to PPh_3 and BPh_4. In the ^1H NMR spectra of methyl derivatives IV and V, the signals of the singlets Cp^1 and Cp^2 disappear.

The ^1H NMR (pyridine-d_5) spectrum of compound VI contains a singlet at 4.9 (Cp) and a multiplet at 5.7 ppm corresponding to five protons of the phenyl ring π-bonded to an atom of ruthenium.

(iii) The IR (KBr) spectra of compounds II–VII have a set of signals in the range 1380–1500 cm^{-1} corresponding to the C–C vibration of the phenyl ring π-bonded to an atom of ruthenium. For compounds II and IV, in the far IR (Nujol) ν(Ru–Cl) 280 cm^{-1} vw was found.

(iv) The mass spectrum (FD) of compound II has the signal of the parent ion at m/e 893 (for ^{102}Ru and ^{35}Cl) whereas for compound III the signal of the parent ion appears at m/e 985 (for ^{127}I). There are also $[II-^{35}Cl]^+$ and $[III-^{127}I]^+$ fragments. In both cases a signal occurs at m/e 429, corresponding to the fragment $[CpRu(\eta\text{-}C_6H_5)PPh_2]^+$. Using a substrate with a methyl group in the cyclopentadienyl ring, a derivative IV is obtained whose mass spectrum contains the expected signal of the parent ion at m/e 921.

When the mixture $CpRuCl(PPh_3)_2$ and its methyl derivative $(\eta\text{-}C_5H_4Me\text{-}(RuCl)PPh_3)_2$ is used in the obtained compounds IV and V, the cyclopentadienyl ring with a methyl group places itself firstly at the ruthenium atom which is already π-bonded to the phenyl ring. On the other hand, introduction of the methyl group to Cp facilitates the formation of the ruthenium bond with the phenyl ring. Also the

yields of compound VII in relation to compound VI are many times higher, as expected from the ratio of the methyl derivative in the substrate to $CpRuCl(PPh_3)_2$.

Conclusions

From the literature data it can be seen that as a result of the dissolution of $CpRuCl(PPh_3)_2$ in MeOH, a solvated cation, $[CpRu(MeOH)(PPh_3)_2]^+$, is formed [2,8]. Thus, the process of dissolution of $CpRuCl(PPh_3)_2$ in methanol may also occur with the formation of $Cp^1RuCl(PPh_3)PPh_2Cp^2Ru^+(\eta\text{-}C_6H_5)Cl^-$, eq. 1. After removal of MeOH, a mixture was obtained containing compound I, substrate $CpRuCl(PPh_3)_2$ and Ph_3PO, as indicated by the ^{31}P NMR spectrum. The amounts of compound I and Ph_3PO (formed from PPh_3) confirm eq. 1. The action of the solution of $NaBPh_4$ on the obtained mixture gives compound II.

Using ethylene glycol instead of MeOH in the dissolution of $CpRuCl(PPh_3)_2$ (reflux) causes a solution (see Experimental, "*v*") containing compound I but not containing the cation $[CpRu(\eta\text{-}C_6H_5)PPh_2]^+$ to be obtained, as shown in the ^{31}P NMR spectrum. This spectrum also contains another signal, an intensive singlet at +32.0 ppm, to which the solvated cation $[CpRu(solv)(PPh_3)_2]^+$ was assigned. However a signal indicating the presence of $CpRuCl(PPh_3)_2$ was not found. The action of $NaBPh_4$ solution on the obtained mixture gives, in this case, tetraphenylborates II and VI. Therefore compound VI forms as a result of decomposition and rearrangement of hypothetical $[CpRu(solv)(PPh_3)_2]BPh_4$.

During longer reflux times (Fig. 1) the molecule of ethylene glycol decomposes with the formation of the CO ligand, to give the cation $[CpRu(CO)(PPh_3)_2]^+$, which is isolated in the form of a stable tetraphenylborate.

Experimental

The reactions were carried out under argon. ^1H NMR spectra were recorded at 60 and 80 MHz using Tesla spectrometers. The ^1H-decoupled ^{31}P NMR spectra were recorded on a JEOL JNM-FX 60 (24.2 MHz) and a Bruker HFX 72 (36.4 MHz) apparatus. H_3PO_4 was used as the external reference. Chemical shifts downfield of the reference have a positive sign. Mass spectra were recorded on a Varian MAT 711 mass spectrometer using the FD technique at 8 + 3 kV and on an LKB Bromma 2091 MS(EI) at variable ionizing voltage. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer using KBr pellets and nujol mulls. Melting points were measured in sealed capillaries and are uncorrected.

i CpRuCl(PPh$_3$)$_2$/ethylene glycol system

0.26 g of $CpRuCl(PPh_3)_2$ and 25 cm^3 of ethylene glycol were refluxed within the time range 0.004–90 h. From the post-reaction mixture, PPh_3, $RuCp_2$, $CpRuCl(PPh_3)_2$ (substrate), $CpRuCl(CO)PPh_3$ and $CpRuH(CO)PPh_3$ were extracted using benzene. To the remaining glycol phase, 50 cm^3 of MeOH and 0.2 g of $NaBPh_4$ in 5 cm^3 of MeOH were added. In the resulting precipitate II, VI and $[CpRu(CO)(PPh_3)_2]BPh_4$ were determined. The yields of these compounds against reflux time are shown in Fig. 1.

ii Preparation of $[CpRu(CO)(PPh_3)_2]BPh_4$ *and* $[(\eta\text{-}C_5H_4Me)Ru(CO)(PPh_3)_2]BPh_4$

0.577 g of $CpRuCl(PPh_3)_2$ and 25 cm^3 of ethylene glycol were refluxed for 6 h. 1 cm^3 of a colourless liquid was distilled off (water, ruthenocene, phosphoroorganic compounds). The glycol phase was extracted using benzene (50 and 25 cm^3), rejecting the extacts. To the remaining glycol phase, 50 cm^3 of EtOH and 0.3 g of $NaBPh_4$ in 5 cm^3 of EtOH were added. The resulting white precipitate was filtered after 10 min. 0.485 g of $[CpRu(CO)(PPh_3)_2]BPh_4$ (59% yield) was obtained. Using MeOH instead of EtOH causes the yield to decrease by several per cent. M.p. 216–224°C (lit. 226–227°C, [7]). ^{31}P NMR (CH_2Cl_2) δ +41.2 (s). Using $(\eta\text{-}C_5H_4Me)RuCl(PPh_3)_2$ instead of $CpRuCl(PPh_3)_2$ results in the formation of yellow $[(\eta\text{-}C_5H_4Me)Ru(CO)(PPh_3)_2]BPh_4$, ^{31}P NMR(CH_2Cl_2)δ +41.9 (s).

iii Preparation of $CpRuCl(CO)PPh_3$ *and* $CpRuH(CO)PPh_3$

The combined benzene extracts obtained according to (ii) were evaporated and separated on a column (silica gel, benzene). The first colourless fraction contained 0.0138 g of $CpRuH(CO)PPh_3$ (3% yield, m.p. 135–140°C). After evaporation of the lemon-yellow second fraction, yellow crystals of $CpRuCl(CO)PPh_3$ (0.0117 g, 3% yield, m.p. 220–222°C) crystallized. ^{31}P NMR ($CHCl_3$)δ +48.4 (s). ^1H NMR, MS(FD) data and the determination of the structure of the compound by X-ray analysis indicated the identity of this compound with the $CpRuCl(CO)PPh_3$ compound obtained by Blackmore et al. [7].

iv Preparation of $CpRu(\eta\text{-}C_6H_5)BPh_3$ *(VIII)*

0.553 g of $CpRuCl(PPh_3)_2$ and 50 cm^3 of diethylene glycol dimethyl ether (diglyme) were refluxed for 4 min. Next 100 cm^3 of MeOH and 0.6 g of $NaBPh_4$ in 5 cm^3 of MeOH were added. The resulting orange-yellow solution was left for 24 h at room temperature. 0.02 g of $CpRuCl(PPh_3)_2$ (substrate) was filtered off and the filtrate was stored for 26 days. After this time, colourless crystals of $CpRu(\eta\text{-}C_6H_5)BPh_3$ (0.181 g, 49% yield, m.p. 292–294°C) were filtered off. MS(FD) *m/e* 486. Prolongation of the storage time (2–3 months) did not cause an increase in the yield of compound VIII.

v Preparation of $[Cp^1RuCl(PPh_3)PPh_2Cp^2Ru(\eta\text{-}C_6H_5)]BPh_4$ *(II) and* $[CpRu(\eta\text{-}C_6H_5)PPh_2]BPh_4$ *(VI)*

3.912 g of powdered $CpRuCl(PPh_3)_2$ and 300 cm^3 of ethylene glycol were heated at boiling temperature for 1 min. After fast cooling to room temperature, 500 cm^3 of MeOH was added. The yellow-orange solution obtained was stored for 3 days at room temperature, with occasional stirring. A yellow-orange precipitate of $CpRuCl(PPh_3)_2$ (1.287 g, 33% recovery) was filtered. To the cleared filtrate a solution of 1.8 g $NaBPh_4$ in 20 cm^3 MeOH was added. As a result, a precipitate containing II and VI was filtered after 1 day. After washing the precipitate with MeOH and drying, 1.411 g of a mixture of II and VI was obtained. Compound II was extracted from the precipitate with chloroform (25 cm^3) and the dark-yellow filtrate obtained was evaporated at 30°C to give 0.698 g of $II \cdot CHCl_3$ in the form of a lemon-yellow precipitate (19% yield).

Crystallization of precipitate II can be carried out in two ways.

(a) 0.063 g of II was dissolved in 3 cm^3 diglyme and 5 cm^3 MeOH. After 14 d of storage, yellow-brown crystals of II were filtered (0.005 g). IR(KBr) 3057m, 3000w,

2988w, 2926w, 1571m, 1472s, 1430s, 1411w, 1386w, 1268w, 1185w, 1151w, 1094m, 1070w, 1035w, 1004w, 921vw, 858s, 813m, 755m, 742s, 712vs, 613m, 589w, 534w, 522s, 513w, 493w, 463m, 444w, 418w.

By changing the composition of the solution, higher yields of compound II can be obtained. 0.698 g of II was dissolved in 10 cm^3 diglyme and 10 cm^3 MeOH. Next the solution was rendered turbid using drops of MeOH and returned to clarity by the use of one drop of diglyme. After 3 days, a yellow substance (0.408 g; m.p. 178–187°C) was filtered off.

(b) From the solution of II · $CHCl_3$ in pyridine, compound II was precipitated using MeOH. The IR(KBr) spectra of the compounds obtained above are practically identical.

^1H NMR($CDCl_3$) spectrum 4.03 (s) Cp^1, 4.31 (s) Cp^2, 5.6 (m) and 4.8 (m) (η-C_6H_5), 7.12 (m), 6.89 (m), 6.79 (m) PPh_3, PPh_2, BPh_4. The ^1H NMR spectrum was taken some hours after the preparation of solution II in $CDCl_3$ using the external reference. The location of the signals in the spectrum was recalculated with respect to the internal reference HMDSO.

The white precipitate obtained after washing the mixture II and VI with chloroform was compound VI (0.681 g, 17% yield). To recrystallize compound VI, the substance was dissolved in 15 cm^3 of pyridine, filtered and 5.5 cm^3 H_2O was added. The suspension was stored for 3 days and then white-yellow crystals of compound VI were filtered and washed with water and MeOH. Ater drying 0.545 g of VI was obtained. M.p. 225–231°C. IR(KBr) 3053m, 3000w, 2984vw, 2926w, 2851w, 1569w, 1470m, 1427m, 1410w, 1385w, 1320vw, 1311vw, 1280w, 1268w, 1180w, 1150w, 1095vw, 1070w, 1030w, 1005w, 925w, 852vs, 752s, 740s, 718s, 662vw, 625w, 615w, 604s, 530w, 500w, 435m.

vi Preparation of IV–VII using methyl derivative of the substrate

3.023 g of a mixture containing 70% (η-C_5H_4Me)$RuCl(PPh_3)_2$ and 30% $CpRuCl(PPh_3)_2$ and 300 cm^3 ethylene glycol were heated at boiling temperature for 1 min. After cooling the solution, 500 cm^3 MeOH was added and after 4 days of storage the isolated substrate mixture (0.528 g, 18% recovery) containing 60% (η-C_5H_4Me)$RuCl(PPh_3)_2$ and 40% $CpRuCl(PPh_3)_2$ was filtered. To the filtrate, a solution of 1.4 g $NaBPh_4$ in 20 cm^3 MeOH was added and after 1 day of storage a precipitate containing IV and V (0.930 g, 37% yield) was filtered. To the dry substance obtained, 25 cm^3 of chloroform was added and after filtration, the filtrate was evaporated at 30°C, yielding 1.021 g (IV and V)·$CHCl_3$ in the form of yellow-gold flakes. The mass spectrum of this compound had signal groups, with maxima at *m/e* 921 (IV), 907 (V) and a weak signal at 893 (trace of II). From the ^1H NMR($CDCl_3$) spectrum and the ratio signal intensity at 4.0 and 4.3 ppm, the ratio Cp^1/Cp^2 could be determined. In the range 1.73–1.60 ppm, signals of methyl groups connected with Cp^1 and Cp^2 were present. The obtained mixture contained approximately 40% IV and 60% V.

The filtrate, after removal of IV and V (volume ca 820 cm^3), was evaporated to half the initial volume, and after 2 h of storage the yellow precipitate was filtered, washed with MeOH and dried, yielding 1.405 g of a mixture, containing IV, V and VII. Using 20 cm^3 of chloroform IV and V were extracted from the mixture, giving 0.848 g (IV and V)·$CHCl_3$ (30% yield). The white precipitate obtained after washing the substance with chloroform was in practice the pure compound VII (13% yield).

When a substrate mixture containing 50% (η-C_5H_4Me)$RuCl(PPh_3)_2$ and 50% $CpRuCl(PPh_3)_2$ was used for the synthesis, a mixture of VI and VII (9% yield) containing 80% of compound VII and 20% of compound VI was obtained.

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