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Cyclopentadienyl-ruthenium and -osmium complexes

VIII *. Formation mechanism of the new [diphenylborato-bis(η^5-cyclopentadienyl,η^6-phenyl-ruthenium(II))]$^+$ cation

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Abstract

Further MS(FD) investigations of CpRu(η^6-C_6H_5)BPh_3 have revealed under increased heating current of the field ion emitter the next set of signals centered at *m/e* 652. To account for this phenomenon, the formation of the dinuclear [(CpRu(η^6-C_6H_5))$_2BPh_2$]$^+$ cation containing two Cp rings, is proposed.

The rearrangement of CpRu(η^6-C_6H_5)BPh_3 into a new ion-pair with [(CpRu(η^6-C_6H_5))$_2BPh_2$]$^+$ cation is also observed in high-boiling point media, such as ethylene glycol. The ion-pair with the tetraphenylborate anion (yield 35%), has been isolated from the reaction. The duration of refluxing was extremely long (100–700 hours). The new ion-pair with BPh_4^- anion is stable and its MS(FD) spectrum shows only the set of signals centered at *m/e* 652.

The mechanism for the synthesis CpRu(η^6-C_6H_5)BPh_3 and its novel complex cation and their MS(FD) investigations are presented.

Introduction

The MS(FD) studies [1] of CpRu(η^6-C_6H_5)BPh_3 (I) as the starting compound, showed that while increasing the heating current of the field ion emitter, a new set of signals centered at *m/e* 652 appeared. This phenomenon was explained in terms of the creation of the new aromatic bond between the intermediate $CpRu^+$ cation and the phenyl ring.

As an extension to the above supposition, it is possible that every dissociation process gives the $CpRu^+$ cation, which can be solvated by the nearest phenyl ring, and finally gives the new, stable, extended cation.

* For part VII see ref. 1.

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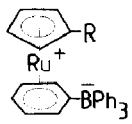
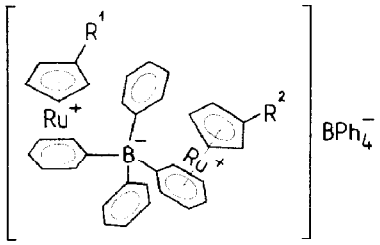




	R	m/e		R^1	R^2	m/e
I	H	486	III	H	H	652
II	CH_3	500	IV	H	CH_3	666
			V	CH_3	CH_3	680

Unexpectedly, it was found that a similar process occurs during the prolonged heating of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ in boiling polar media, (such as ethylene glycol, b.p. 197 °C) under reflux. The cation obtained, [diphenylborato-bis(η^5-cyclopentadienyl,η^6-phenyl-ruthenium)]$^+$, a sparingly soluble ion-pair with the tetraphenylborate anion, can be isolated from the ethylene glycol/methanol mixture. The use of the partially methylated substrate under further reflux gave sets of signals centered at *m/e* 652, 666 and 680, in the MS(FD) spectrum, in accord with the proposed formulae.

Synthesis of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$

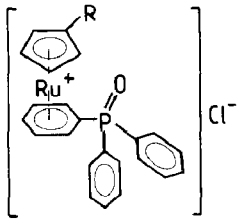
In 1971 $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ was isolated by Haines and du Preez [2]. Three years later the structure of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ was determined by X-ray diffraction [3]. The reaction of $CpRuCl(PPh_3)_2$ with $NaBPh_4$ in methanol (under reflux for 14 hours) followed by the concentration and storage of the obtained solution, gives brown crystals of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (I) in 20% yield [3]. $CpRuCl(CO)_2$ is used in place of $CpRuCl(PPh_3)_2$ only $CpRu(\sigma\text{-}C_6H_5)(CO)_2$ is formed and not $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ [2].

The best method for preparation of the $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ is probably the reaction of $CpRuCl(PPh_3)_2$ with $NaBPh_4$ in diglyme-methanol mixture, which gives colourless crystals in about 70% yield [4] (Experimental i).

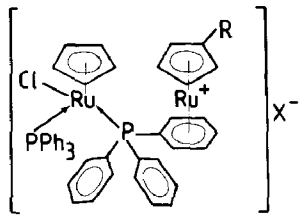
Further studies have indicated that a small amount of oxygen in the system is required to start the synthesis of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ at room temperature. If air is rigorously excluded from the $CpRuCl(PPh_3)_2$/$NaBPh_4$/diglyme-MeOH system, no reaction takes place, even after storage for three months. If a small amount of air is introduced $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ is formed in 60% yield (Experimental ii).

When $CpRuCl(PPh_3)_2$ is refluxed in diethylene glycol dimethyl ether (diglyme) in presence of a little air, a solution containing mainly unchanged $CpRuCl(PPh_3)_2$ and small amount of $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]Cl$ (VI) is obtained, as can be seen from ^{31}P NMR spectrum (signals at 38.4 ppm and 26.1 ppm, respectively). The presence of VI in solution confirms the action by air [5].

In contrast, when $CpRuCl(PPh_3)_2$ is refluxed for a short time in ethylene glycol then diluted with methanol, a solution containing the dinuclear compound, VIII, is



	R
VI	H
VII	CH_3



	R	X
VIII	H (or CH_3)	Cl
IX	H (or CH_3)	BPh_4

obtained, which shows the characteristic doublet of doublets in the ^{31}P NMR spectrum. In addition the signal from $Ph_3P{=}O$ is present in this spectrum, which confirms the action by oxygen, because no special precautions were taken to exclude air during work-up. But traces of oxygen in the system are not required for the synthesis of compound VIII. However, during the reflux of $CpRuCl(PPh_3)_2$ in low boiling point alcohols (such as methanol) the presence of oxygen is required to give VIII. Thus it is not surprising that $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ results from the rearrangement of the ion-pair containing the tetraphenylborate anion (IX) at room temperature:

$$IX\ (diglyme/MeOH) \rightarrow CpRu(\eta^6\text{-}C_6H_5)BPh_3 \downarrow \quad (1)$$

The choice of the diglyme/MeOH mixture utilizes the good solubility of the starting compound IX and the poor solubility of the final $CpRu(\eta^6\text{-}C_6H_5)BPh_3$.

In fact, during the storage of compound IX in the solution $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ separates out [4], and MS(FD) investigations of compound IX show signals centered at *m/e* 486, which confirm that $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ is present.

Compounds such as VIII can be obtained by:

(i) heating of $CpRuCl(PPh_3)_2$ in low boiling point alcohols under reflux (methanol, ethanol) in presence of oxygen [5], or by

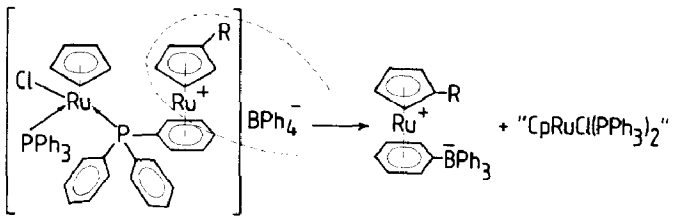
(ii) heating of $CpRuCl(PPh_3)_2$ in high boiling point glycols under reflux (such as ethylene glycol); oxygen is not required [4].

For both (i) and (ii) the formation of the intermediate $CpRu^+$ cation as a result of the dissociation process of $CpRuCl(PPh_3)_2$ is postulated.

It is well-known [6] that the replacement of both the carbonyl ligands in $CpRuX(CO)_2$ (X = halogen) is extremely difficult compared to that of $CpRuCl(PPh_3)_2$. Thus, the formation of the $CpRu^+$ cation is more probable in the case of $CpRuCl(PPh_3)_2$ than in that of $CpRuCl(CO)_2$. This explains why $CpRuCl(CO)_2$ and $NaBPh_4$ do not give $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ [2].

The proposed mechanism of the formation of the compounds $(\eta^5\text{-}C_5H_4R)Ru(\eta^6\text{-}C_6H_5)BPh_3$ is shown in Scheme 1. Displacement of the intermediate $(\eta^5\text{-}C_5H_4R)Ru^+$ group to the tetraphenylborate anion finally gives II. The methyl-cyclopentadienyl-ruthenium group migrates to the tetraphenylborate anion to give compound II and not the non-methylated compound I (Scheme 1). Formally, in this process the non-methylated $CpRuCl(PPh_3)_2$ molecule should be regenerated.

To demonstrate the origin of the cyclopentadienyl group in $CpRu(\eta^6\text{-}C_6H_5)BPh_3$, MS(FD) investigations of IX containing two different cyclopentadienyl groups were



R=CH3 (IX) (II)

Scheme 1

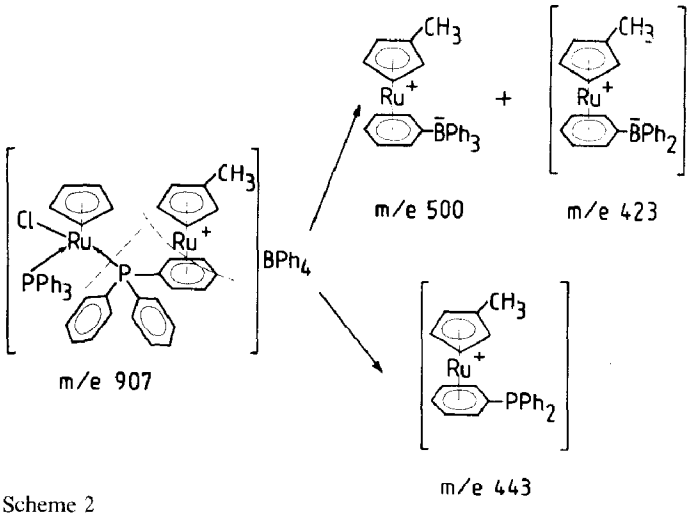
carried out. One of two groups is methylated and it is located at ruthenium atom which is π-bonded to phenyl ring of one of the PPh_3 ligands.

The MS(FD) spectrum shows a main signal at *m/e* 500, which corresponds to compound II. Therefore methylated species at *m/e* 443 and *m/e* 423 which are formed as a result of fragmentation of the starting complex IX and the product II respectively, also were noted. The presence of the above fragments in MS(FD) spectrum explains why the $CpRuCl(PPh_3)_2$ signal cannot be observed, because of its prior fragmentation. Similarly, when compound IX is stored in solution, no $CpRuCl(PPh_3)_2$ is detected in the postreaction mixture. The $(\eta^5\text{-}C_5H_4CH_3)Ru(\eta^6\text{-}C_6H_5)BPh_3$ (II) should be formed with more difficulty than $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (I), because of:

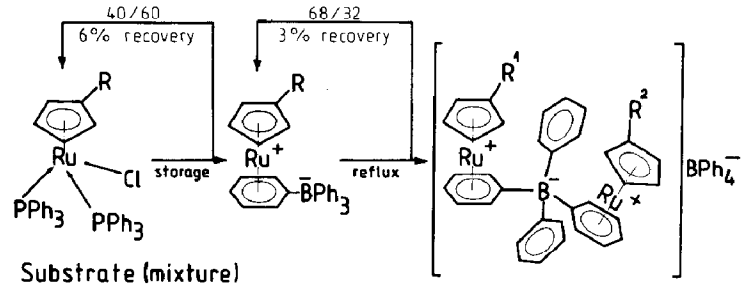
(i) the formation of a stronger bond between the $(\eta^5\text{-}C_5H_4CH_3)Ru^+$ group and the phenyl ring of $CpRuCl(PPh_3)_2$ molecule in IX [4], and

(ii) because of the increase in the electronegativity of $(\eta^5\text{-}C_5H_4CH_3)Ru^+$ group in comparison with $CpRu^+$ [1] which causes the less probable attack on the phenyl ring of the tetraphenylborate anion.

The above supposition was confirmed by MS(FD) studies of compounds $[(\eta^5\text{-}C_5H_4R)Ru(\eta^6\text{-}C_6H_5)PPh_2]BPh_4$. In the case where $R = CH_3$ only a small signal at

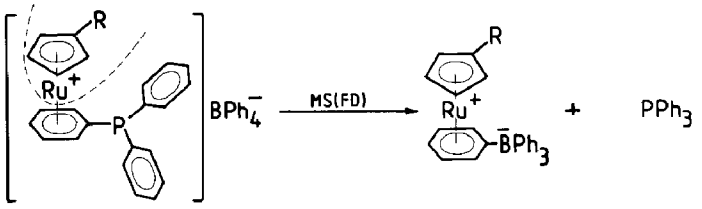


Scheme 2



100%			20% yield			7% yield			
Mixture ratio						%	48	40	12
%	50	50	%	68	32	R^1	H	H	CH_3
R	H	CH_3	R	H	CH_3	R^2	H	CH_3	CH_3
						Average %	68	32	
						R	H	CH_3	

Scheme 3



R=H	m/e 429	486	262
$R=CH_3$	m/e 443	500 (insignificant)	—

Scheme 4

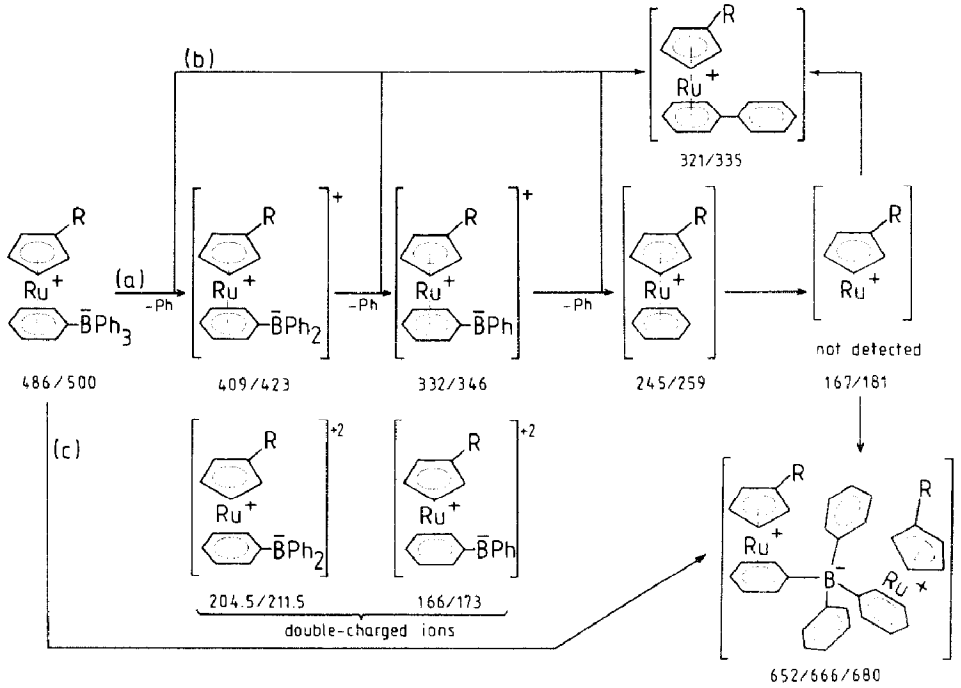
m/e 500 (corresponding to II) was observed. Practically only the signal of the parent ions of the starting compound (at *m/e* 443) was detected.

The possibility remains open that $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ formation occurs with omission of the postulated intermediate stage connected with the rearrangement of the ion-pair containing the tetraphenylborate anion (such as IX, Scheme 1). But the experimental data indicate that the methyl substituent in the Cp-ring in $(\eta^5\text{-}C_5H_4CH_3)RuCl(PPh_3)_2$ facilitates the formation of $[(\eta^5\text{-}C_5H_4CH_3)Ru]^+$, which is followed by the creation of a ruthenium π-bond with the phenyl ring. The much higher field of compound VII, compared with that of VI, than expected from the proportion of methyl derivative to $CpRuCl(PPh_3)_2$ in the substrate mixture (cf. [4]) confirms the above.

In conclusion, the introduction of the methyl substituent into the Cp ring should increase methyl product (II) formation, but in practice it does not.

MS(FD) studies of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$

When the heating current of the field ion emitter is increased several new sets of signals appear in the MS(FD) spectra of I and II, in addition to the expected parent ions signals (at *m/e* 486 and 500, respectively).



Scheme 5. The m/e values for R = H are on the left of the solidus; those for R = CH_3 are on the right.

The MS(FD) studies for the starting mixture of I and II are depicted in Scheme 5. The intense signal at m/e 409 (or m/e 423 for R = CH_3) is the result of the removal of one phenyl group (C_6H_5) from the starting compounds (pathway a, Scheme 5).

As an exception the $[CpRu(\eta^6\text{-}C_6H_5)BPh_2]^+$ and $[CpRu(\eta^6\text{-}C_6H_5)BPh]^+$ fragments are present in addition to the single-charged ions (m/e centre at 409 and 332, respectively) and as double-charged ions (m/e centre at 204.5 and 166, respectively).

The signal at m/e 166 should not be regarded as the signal from the $CpRu^+$ cation (m/e 167) because:

(i) in the mixture with methylated derivates the analogous set of methylated fragments lies at m/e 173, thus this set is shifted by 7 m/e unit, and not by 14;
(ii) the signals are of double density per m/e unit, compared with the single signal density per m/e unit in the case of single-charged ions.

Thus, in the above process (Scheme 5) both intermediate species $CpRu^+$ and C_6H_5 form the $[CpRu(\eta^6\text{-}C_6H_5)Ph]^+$ cation:

$$CpRu^+ + 2\ C_6H_5 \rightarrow [CpRu(\eta^6\text{-}C_6H_5)Ph]^+ \qquad (2)$$

The above cation was obtained on a preparative scale by Nesmeyanov et al. in 1979 by an exchange reaction of ruthenocene with diphenyl; in the presence of aluminium chloride [7]. In addition Vol'kenau et al. obtained this cation in 1984 from the reaction of *exo*-phenylcyclohexadienyl-cyclopentadienylruthenium with *N*-bromosuccinimide in the presence of $NaPF_6$ [8].

Similarly, the interaction of the intermediate $CpRu^+$ cation with starting I and II (Scheme 5, pathway c) gives the new complex cations (m/e 652, and for R = CH_3 m/e 666 and 680).

$CpRu(\eta^6\text{-}C_6H_5)BPh_3$ ethylene glycol system

The solution of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (Experimental iii) in ethylene glycol under reflux during 30–700 hours also gives the [diphenylborato-bis(η^5-cyclopentadienyl-η^6-phenylruthenium)]$^+$ cation. After the dilution of the reaction mixture with methanol, followed by the addition of $NaBPh_4$, the sparingly soluble ion-pair (III) was isolated (Fig. 1) in up to ca. 35% yield.

In the MS(FD) spectrum, III appears only as the set of signals centered at *m/e* 652. The value *m/e* 652 in has been observed in the computer simulation FD spectrum for the formulation $C_{34}H_{30}BRu_2$. A mixture of I and II heated under reflux in ethylene glycol, should give the expected mixture of differing tetraphenylborates (III–V) after the addition of $NaBPh_4$. In the mass spectra of compounds III–V only the expected groups of signals at *m/e* 652, 666 and 680 are present, without the signals at *m/e* 486 and 500, which confirms that starting I and II are not present in the product mixture.

It is not the methyl substituent at the Cp ring that affects the ratio of the yields of the methylated and non-methylated products in regard to the substrate mixture used (Scheme 3) but the large and unexpected difference compared to the process of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ synthesis.

Furthermore, it has been observed that the product of prolonged refluxing, isolated as the sparingly soluble tetraphenylborates also contains small amounts of other compounds which, in the MS(FD) spectrum, give repeated sets of signals, similar in shape but shifted in relation to the main set (*m/e* values 652, 666 and 680) by 76 *m/e* units.

Scheme 6 shows the various cationic products formed during the prolonged refluxing of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$, isolated as a sparingly soluble tetraphenylborate mixture. The origin of the sets of signals in the MS(FD) spectrum of the mixture apart from the major set of signals at *m/e* 652, 666, and 680) has been ascribed to the removal and migration of the phenyl group (C_6H_5). The intensities of the signals are insignificant and are less than 10% of those of the major signals. In addition, the

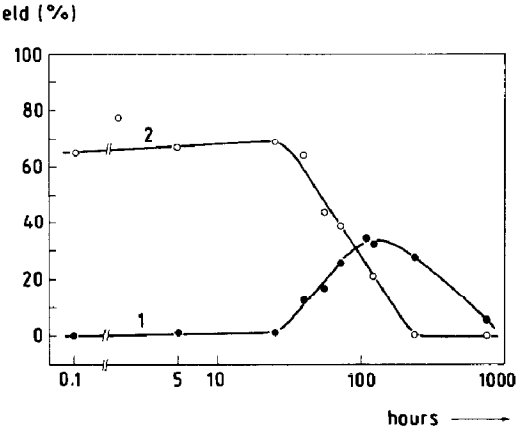
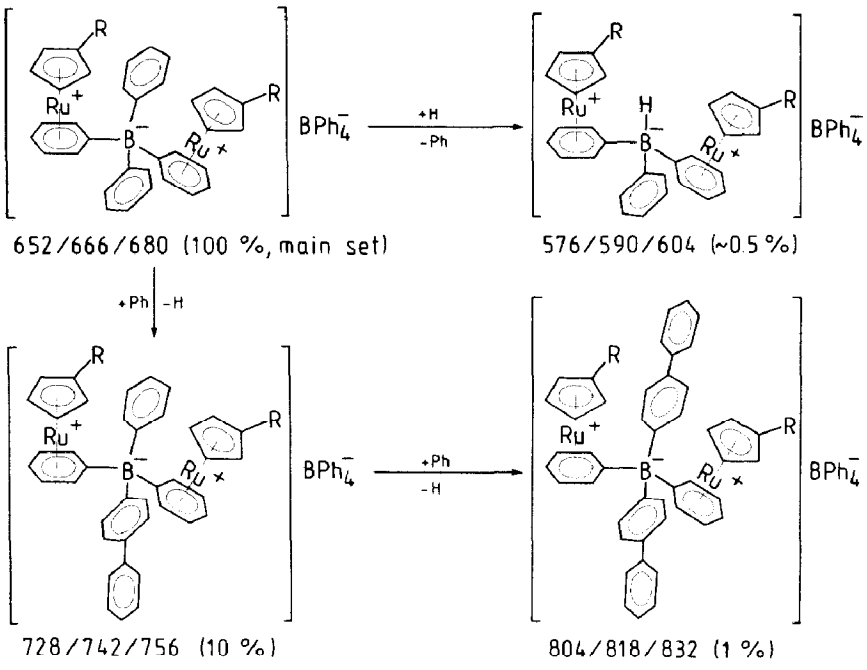


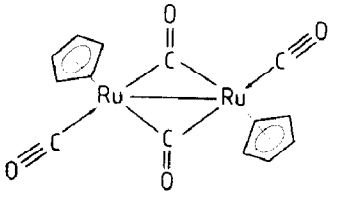
Fig. 1. The relationship between the yields and the refluxing time of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ substrate in ethylene glycol medium. Curve 1 (●): the yields of compound III; curve 2 (○): substrate recovered.



Scheme 6

methyl substituent in the Cp ring had no effect on the ratio of methylated and non-methylated products in regard to the used substrate mixture.

The process, that follows occurs during the prolonged refluxing of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ in ethylene glycol and yields tetracarbonyl-bis(η^5-cyclopentadienyl)di-ruthenium (X):



X

Ethylene glycol acts as a source of carbon monoxide ligand. The decarbonylation of the alcohols by triphenylphosphine ruthenium complexes is well known [9]. In addition the high boiling point glycols are good donors of carbon monoxide [4] and the reaction that takes place during refluxing competes strongly with the oxidation of PPh_3 by oxygen. For example, the reflux of $CpRuCl(PPh_3)_2$ in ethylene glycol during several hours under simultaneous bubbling of air through the mixture, gives the cationic carbonyl derivates of ruthenium $[CpRu(CO)(PPh_3)_2]^+$ as the main product in 36% yield and the oxidation product of the triphenylphosphine $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]^+$ in only 3% yield (Experimental iv).

The yield of $[CpRu(CO)_2]_2$ (X), which forms during more prolonged reflux $CpRu(\eta^6\text{-}C_6H_5)BPh_3$, depends strongly on the reaction conditions. Compound X

(*trans* isomer) condenses as orange-yellow crystals on the cold area of the reflux condenser (Experimental iii).

To explain the synthetic process of III the simplest mechanism based on the stoichiometrical suppositions must be rejected:

$$2\ CpRu(\eta^6\text{-}C_6H_5)BPh_3\ (I) \rightarrow [(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]BPh_4 \qquad (3)$$

After refluxing for up to 240 hours, only the substrate $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (max. recovery 70%, Fig. 1) precipitates, not complex III. The addition of $NaBPh_4$ to the post-reaction mixture necessitates the isolation of the product as the sparingly soluble ion-pair with tetraphenylborate anion (III), which indicates that the BPh_4^- anion is not liberated during reflux. The starting compound $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ probably undergoes a gradual, step-by-step degradation, to give the unsolvated $CpRu^+$ cation. This assumption is confirmed by MS(FD) studies (Scheme 5).

The stepwise, intermediate species detected during the investigations of the compounds $CpRu(\eta^6\text{-}C_6H_5)BPh_3$, are presented in Scheme 5. In contrast to the previously presented mechanism of synthesis of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ as a single-stage substitution of $CpRu^+$ group for the tetraphenylborate anion (Scheme 1), the synthesis of III is proceeds by the sequential degradation of the $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ to $CpRu^+$ and finally, the reaction of $CpRu^+$ with intact $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ molecules. Of course, the addition of the $NaBPh_4$ solution to isolate the sparingly soluble ion-pair, III is still necessary.

The signal at *m/e* 167 corresponding to $CpRu^+$ cation is not present in the MS(FD) spectrum because it reacts with the nearest phenyl ring to form a stable π bond. It is probable that a similar mechanism operates during the prolonged reflux of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ in high boiling point glycols.

^{1}H NMR investigations

Comparative data for $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (I) and $[(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]$-$BPh_4$ (III) in deuterated pyridine and dimethyl sulfoxide are listed in Table 1. The Cp resonance occurs between 4.61 and 4.70 (pyridine-d_5) for I and III, respectively.

Table 1

^{1}H NMR data for $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (I) and $[(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]BPh_4$ (III)

Complex	Solvent	δ ppm (TMS)		
		Cp	(η^6-C_6H_5)	B–Ph
I	C_5D_5N	4.61 (s)	6.10 (m)	7.58 (m)
			5.46 (m)	7.18 (m)
	$(CD_3)_2SO$	4.96 (s)	5.95 (s)	7.19 (m)
				7.10 (m)
				7.01 (m)
III	C_5D_5N	4.70 (s)	5.87 (m)	8.00 (m)
			5.63 (m)	7.30 (m)
				7.13 (m)
	$(CD_3)_2SO$	5.05 (s)	5.98 (m)	7.21 (m)
			5.91 (m)	6.96 (m)
				6.88 (m)

The newly-prepared complex III, which has two Cp rings, also gives a singlet for the Cp resonances. The two Cp rings are equivalent and the signal is shifted slightly downfield relative to that of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$. This observation is consistent with expected influence of the $CpRu^+$ group introduced into the neutral $CpRu(\eta^6\text{-}C_6H_5)BPh_3$. In general, decreased basicity of the donor causes a downfield shift of the resonance. Thus, the $CpRu^+$ group can be regarded as a species of cation because it strongly diminishes the basicity of the $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ molecule.

The $(\eta^6\text{-}C_6H_5)$ resonance occurs between 5.71 and 5.72 ppm (weighted mean for complexes I and III, respectively) and downfield shift is slight. In the case of the ^1H NMR spectra in deuterated DMSO, no shift occurred, Table 1.

All these indicate that the extended $[(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]^+$ single-charged cation, containing two positive-charged centre and one negative-charged centre, is a poorer transmitter of the electronic effects. For example, the introduction of a methyl substituent into one of the two Cp rings, in IV has no effect on the chemical shift of the second, non-methylated Cp ring.

Conclusions

The formation of the new stable $[(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]^+$ cation either in higher vacuum on the emitter MS(FD) device or during prolonged refluxing in high boiling point glycols, is presented. The zwitter-ionic $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ is used as a starting compound, which undergoes sequential degradation, finally to give the $CpRu^+$ cation, which is immediately solvated with phenyl ring of the $CpRu(\eta^6\text{-}C_6H_5)BPh_3$:

$$CpRu(\eta^6\text{-}C_6H_5)BPh_3 + CpRu^+ \rightarrow [(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]^+ \quad (4)$$

In mass spectrometry (MS) under field desorption (FD), ion generation is possible by field ionization (FI) or desolvation. By FI, the molecules are ionized by electron tunnelling, to give the molecular ions. In desolvation, the ions are formed, for example, by the attachment of a proton or of an alkali metal ion to the molecule [10].

Thus, process 4 in the MS(FD) version may be regarded as the attachment of an intermediate $CpRu^+$ cation to the neutral $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ molecule (cation formation). This accounts for the previously mentioned fact that the $CpRu^+$ signal at *m/e* 167 was not found in the MS(FD) spectrum of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$.

It was expected that more prolonged refluxing of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ in glycols by stepwise loss of the fragments from the starting compound should give solely the $CpRu^+$ cation. If no intact $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ is present in the reflux system, the ethylene glycol acts as a source of the carbon monoxide, and it forms the tetracarbonylbis(η^5-cyclopentadienyl)diruthenium(*Ru–Ru*) (X).

Compound X is known [11–16] and is usually prepared by the reaction of $Ru_3(CO)_{12}$ with cyclopentadiene C_5H_6, air is bubbled through the solution to give the desired product in 61% yield [15]. Crystals of this compound were found to have deposited on the cold area of the reflux condenser (Experimental iii) as the *trans* isomer (from its IR spectrum). The differentiation of both $[CpRu(CO)_2]_2$ isomers in the solid state is not difficult; the *cis* isomer shows two terminal $\nu(C{\equiv}O)$ absorptions, whereas the *trans* isomer exhibits only one [15,16].

Experimental

General experimental conditions and apparatus are similar to those described in previous parts of this series. In addition Tesla ^{1}H NMR (100 MHz) and Bruker ^{31}P NMR (121.49 MHz) instruments were used. The $CpRuCl(PPh_3)_2$ resonates at $\delta = +38.34$ ppm (s) in the off-resonance ^{1}H-decoupled ^{31}P NMR spectrum (in chloroform also taken as the internal standard).

i. Preparation of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ (I). A typical preparation, similar to that described previously [4] is outlined. Under apparently identical conditions the yield of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ varied from 40 to 70%. 1.42 g of $CpRuCl(PPh_3)_2$ and 100 cm^3 of diglyme were refluxed under argon for 4 minutes, and to the cooled yellow-orange solution was added 200 cm^3 of MeOH and 1.2 g of sodium tetraphenylborate in 10 cm^3 of MeOH. After two days of storage the well-shaped crystals of substrate (regeneration of 0.2689 g of $CpRuCl(PPh_3)_2$) was filtered off in the presence of air, and the filtrate was stored. It was observed that several hours after filtration, colourless crystals of compound I began to separate from the filtrate. After 8 days of storage, 0.5283 g of compound I (68% yield) were isolated. After 5 months of storage only 0.0254 g of compound I (3% yield) were filtered from the remaining filtrate. The use of $(\eta^5\text{-}C_5H_4CH_3)RuCl(PPh_3)_2$ in place of $CpRuCl(PPh_3)_2$ gives $(\eta^5\text{-}C_5H_4CH_3)Ru(\eta^6\text{-}C_6H_5)BPh_3$ (II), but in the decreased yield (10–20%).

ii. The $CpRuCl(PPh_3)_2$/MeOH/$NaBPh_4$/oxygen system. A mixture of 0.5035 g of $CpRuCl(PPh_3)_2$, 0.60 g of $NaBPh_4$, 50 cm^3 of diglyme, and 100 cm^3 of MeOH under argon was left to stand for three months with rigorous exclusion of air. During this time the reaction had not started and much of the $CpRuCl(PPh_3)_2$ remained undissolved. The introduction of air into the suspension gave I during two further months of storage. During the storage after aeration, the orange crystals of the substrate dissolved and colourless crystals of compound I formed. Finally, the pure product was filtered, to give 0.2028 g of I, m.p. 292–294 °C, 60% yield.

iii. The $CpRu(\eta^6\text{-}C_6H_5)BPh_3$/ethylene glycol system. A mixture 0.080 g of $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ and 10 cm^3 of ethylene glycol were refluxed during 0.1–720 hours. The temperature of the electric heating mantle was stabilized at 202–206 °C. After cooling, 10 cm^3 of MeOH were added and the unchanged $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ was filtered off (if time of reflux was < 260 hours). To the filtrate was added a solution of 0.040 g of $NaBPh_4$ in 2.5 cm^3 of MeOH. After 7 days of storage the crystalline precipitate, III, was filtered off. The relationship of yield against duration of reflux is given in Fig. 1. The $[(CpRu(\eta^6\text{-}C_6H_5))_2BPh_2]BPh_4$ (III) is isolated as colourless, crystals m.p. 249–252 °C. A refluxing time of 110 hours gives III in 35% yield IR(KBr) 3055w, 3040w, 3000w, 2925w, 2850w, 1580m, 1480s, 1445m, 1428m, 1418m, 1395m, 1268m, 1190w, 1150m, 1110w, 1070w, 1035w, 1010w, 846s, 740vs, 712vs, 615vs, 472m, 438m.

Prolonged refluxing yields compound X, which can be isolated from the post-reaction mixture by extraction with benzene or X can be collected from the inside of the reflux condenser. Reflux for 240 hours, gives X in 50% yield of X may be obtained. MS(FD) 445 (parent ion). IR(KBr) 1920vs ν(C≡O), 1740vs ν(C=O), 1400m, 1335m, 1106w, 1055m, 1011m, 994m, 870vw, 840m, 812s, 740m, 680sh, 645vs, 575m, 538m, 517s, 486w.

iv. The $CpRuCl(PPh_3)_2$/ethylene glycol/oxygen system. A solution of 0.8471 g of $CpRuCl(PPh_3)_2$ in 25 cm^3 of ethylene glycol through which a stream of air was slowly bubbled was refluxed for 4 hours. The resulting yellow solution was extracted with benzene (4×25 cm^3). The extracts, were discarded as they contained ruthenocene, (5% yield). After the residual benzene had been evaporated from the glycol phase, 100 cm^3 of MeOH and 1 g of $NaBPh_4$ in 10 cm^3 of MeOH, were added. The precipitate was filtered to give 0.4398 g of a whitish-yellow mixture, containing $[CpRu(CO)(PPh_3)_2]BPh_4$ (36% yield) and $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]BPh_4$ (3% yield), from its ^{31}P NMR spectrum (chloroform), signals at δ 41.45 (s) and δ 25.44 (s) ppm, respectively.

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