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Cyclopentadienyl-ruthenium and -osmium complexes

IX *. Cation formation of cyclopentadienylruthenium complex molecules by the $CpRu^+$ cation during reflux in alcohols or glycols

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Abstract

Information from MS(FD) and (EI) investigations of compounds containing [CpRu] fragment is presented. In a few cases cation formation gives the new extended cations having *m/e* values above those of the starting parent ions, enlarged by a 167 unit. An analogous process, taking into account the final product, can occur during reflux of the starting compounds, e.g. $CpRuX(PPh_3)_2$ type (X = Cl, Br, I) in glycols or lowboiling alcohols. In the last case the access of oxygen, playing the role of the labilizing agent of the PPh_3 ligands, is necessary. The phosphorus NMR studies of the dinuclear cations $[CpRuCl(PPh_3)CpRu(\eta^6\text{-}C_6H_5)PPh_2]^+$ as well as the application of the rule on the effect of the methyl substituent at Cp-ring on changes in the phosphorus NMR spectra, are described in detail.

Introduction

In previous parts of this series [1–3] it was stated that during the MS(FD) investigations of compounds containing the $[CpRu^+]$ moiety, the signal from $CpRu^+$ cation was not found in the spectra. However the $CpRu^+$ species, which forms on the MS(FD) emitter device, immediately reacts with the nearest phenyl ring, to create the new π-bond between the ruthenium atom and phenyl ring [3]. The novel cationic species obtained in this manner have *m/e* values greater than those of the parent ion.

* For part VIII see ref. 3.

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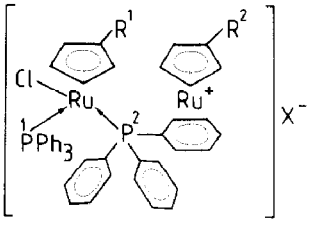
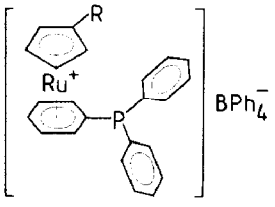


	R^1	R^2	X
I	H	CH_3	BPh_4
II	H	H	BPh_4
III	CH_3	CH_3	BPh_4
IV	CH_3	H	BPh_4
V	H	CH_3	Cl
VI	H	H	Cl
VII	CH_3	CH_3	Cl
VIII	CH_3	H	Cl

The cation formation, mentioned above, can also occur during reflux of the starting compounds in alcohols or glycols [3]. Thus the products of cation formation process of the starting compounds, such as $CpRuX(PPh_3)_2$ type (X = halogen), can be obtained [1]. The sparingly soluble, novel ion-pairs that result from the addition of sodium tetraphenylborate solution to the post-reaction mixture can be readily isolated. If $CpRuCl(PPh_3)_2$ is the starting compound, compounds II or VI are obtained.

The MS(FD) study of $CpRuX(PPh_3)_2$ (X = Cl, Br, I) showed only the main signals of the parent ions and no other larger *m/e* values were observed. In some MS(FD) spectra the signals having m/e values less than those of the parent ion were observed. It is common to observe the signal of triphenylphosphine (*m/e* 262) as a result of $CpRuX(PPh_3)_2$ dissociation (e.g. for X = Br) or a signal at *m/e* 429 from the $[CpRu(\eta^6\text{-}C_6H_5)PPh_2]^+$ cation which is the result of reaction of the $CpRu^+$ species with PPh_3 molecule (for X = Cl), [4]. The latter reaction confirms that $CpRu^+$ is formed as a result of two sequential of decompositions of the starting compounds on the MS(FD) emitter device. But when this process of decomposition, which finally gives the $CpRu^+$ species, is prolonged and no intact molecules of starting compounds are present, then the cation formation process with the $CpRu^+$ cation results in decomposition products having the phenyl ring (e.g. PPh_3 molecule, compound IX).



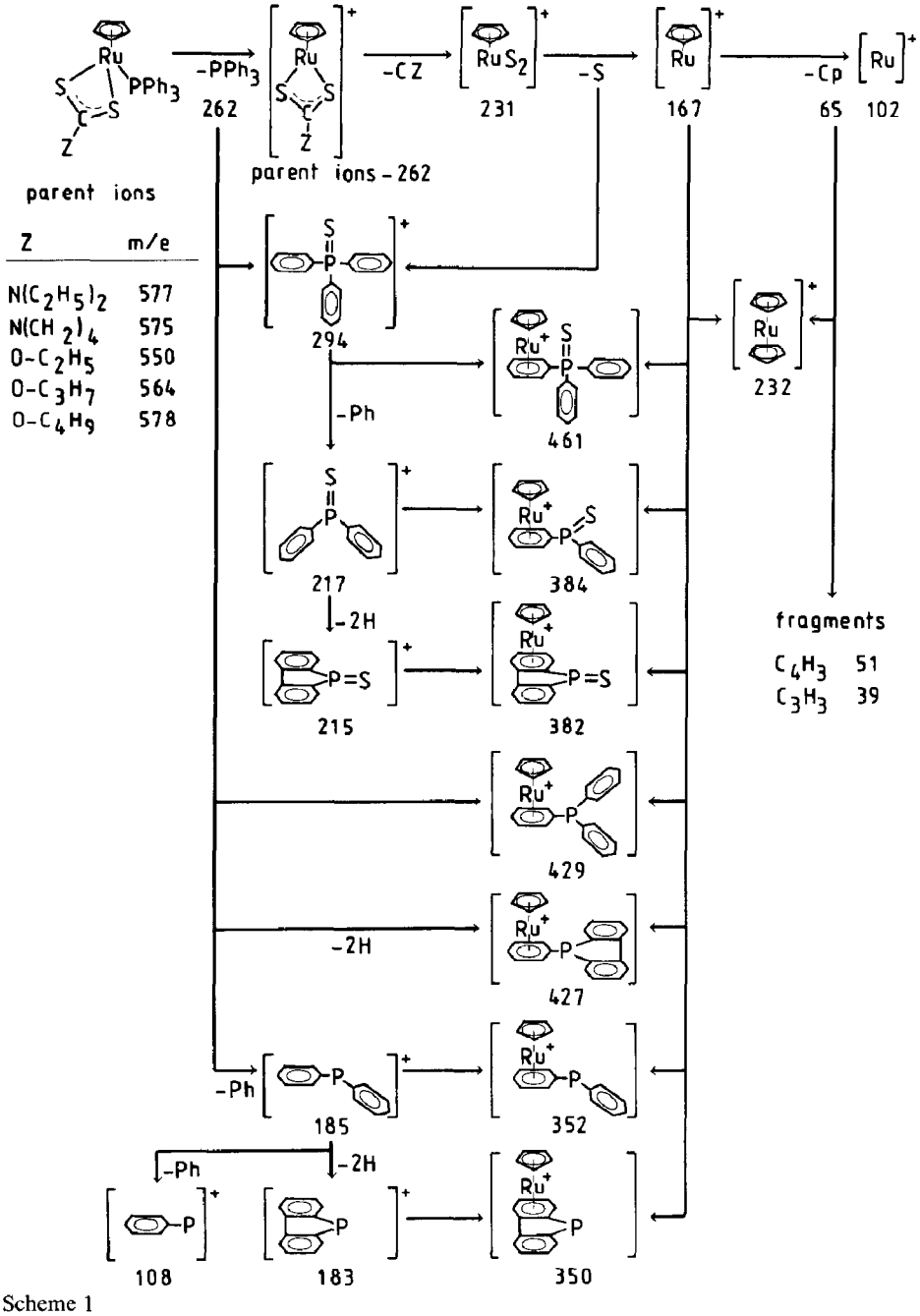
	R
IX	H
X	CH_3

The electron impact technique (EI) renders many organic molecules labile so that they undergo partial or even complete decomposition. In the MS(EI) spectra of complexes containing cyclopentadienyl groups the signal at *m/e* 167 corresponding to the $CpRu^+$ cation is clearly present.

The MS(EI) data for ruthenocene have been published and were found to include that for the $CpRu^+$ signal [5–7]. In the case of the methyl-ruthenocene derivates the signal at *m/e* 181 corresponding to the $(\eta^5\text{-}C_5H_4CH_3)Ru^+$ cation has also been

observed [4]. But the use of the ruthenocene-monocarboxylic acid (or ruthenocene-dicarboxylic acid) as starting compounds shows that the decarboxylation process begins before the fragmentation process. Thus, only the intense signal at *m/e* 44 (corresponding to CO_2) and the signal of the $CpRu^+$ cation (not $[(\eta^5\text{-}C_5H_4COOH)Ru]^+$) are seen [8].

The behaviour of $CpRuX(PPh_3)_2$ complexes is well known. Ions occurring in the MS(EI) spectra correspond to the loss of one PPh_3 ligand and the X group [9]. In



Scheme 1

the MS(EI) spectrum of $CpRuH(CO)_2$, the peak at m/e 167 is the strongest signal [10]. The stages of degradation of the compounds $CpRu(PPh_3)$(dithiocarbamate/xanthate) [11] during MS(EI) at an ionization voltage of 75 V are depicted in Scheme 1. Besides the intense molecular ion signals and a number of other signals in the spectra, there were a number of significant ones at m/e 77, 108, 183, 262 (originating from the PPh_3 molecule) as well at 294 from triphenylphosphine sulfide and at 461 from the $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}S]^+$ cation which is formed by the participation of sulfur and the $CpRu^+$ cation.

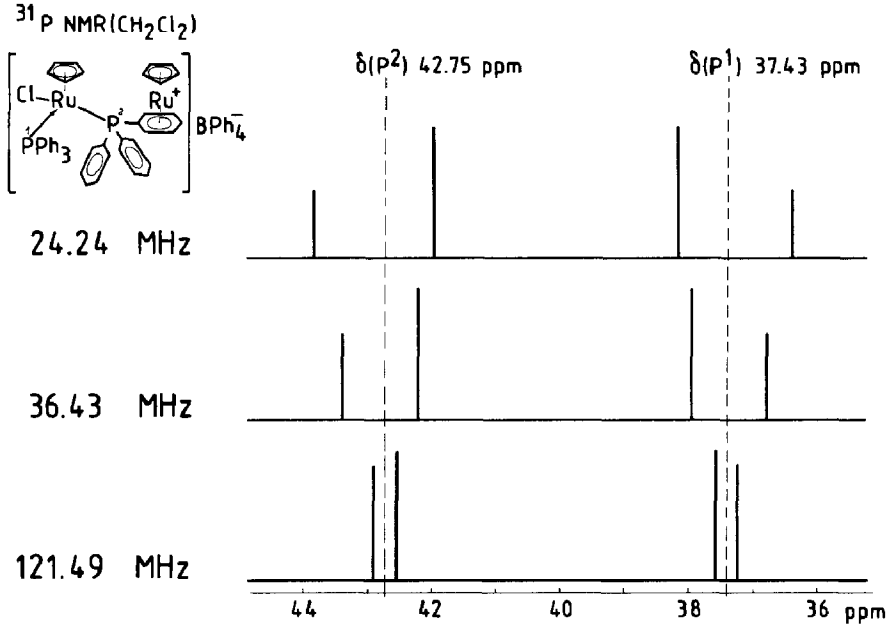
Interestingly, the presence of a strong signal at m/e 183 which originates from the fragmentation product of PPh_3 is connected with loss of phenyl and two hydrogen atoms [12,13]. It is probable that the ion at m/e 427 has a structure consisting of a phenyl ring π-bonded to ruthenium atom rather than being σ-bonded as was suggested by other workers [9,10]. Williams, Ward and Cooks in their excellent work [12], involving mass spectrometry studies of the triphenylphosphine and triphenylphosphine sulfide compounds, have suggested that there are several intermediate stages in the main decomposition pathways. The MS(EI) spectra of the dithiocarbamate and xanthate ruthenium complexes in [11] showed almost all of the fragments mentioned in the literature [12], Scheme 1. In addition the experimental spectra show most of the fragments containing bonded $CpRu^+$ species (m/e values enlarged by 167 units). It is obvious that the competitive reaction with sulfur (only when the starting compound contains sulfur) competes strongly with the oxygen-participation reaction.

In summary, the distinct reactivity of the intermediate $CpRu^+$ cation is evident from the MS(FD) and MS(EI) spectra, except for those for the $CpRuX(PPh_3)_2$ compounds, in which the signals of the cation-formation products with $CpRu^+$ were not found. However reflux in alcohols of compounds of the $CpRuX(PPh_3)_2$ type yielded the expected new extended cations on a preparative scale [1,3].

Results and discussion

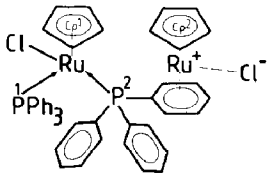
Since the original suggestion [1] in 1985 that $CpRuCl(PPh_3)_2$ in ethylene glycol undergoes chemical dissolution during reflux to give the intermediate $CpRu^+$ cation which immediately reacts with another still intact $CpRuCl(PPh_3)_2$ molecule finally to form the extended $[Cp^1RuCl(PPh_3)Cp^2Ru(\eta^6\text{-}C_6H_5)PPh_2]^+$ cation, further information has appeared. The sparingly soluble ion-pair (compound II can be readily isolated from the post-reaction mixture after the addition of $NaBPh_4$. (Experimental i). The yellow-orange compound II is stable and shows the characteristic doublet of doublets (Scheme 2) in its ^{31}P NMR spectrum. Scheme 2 shows the peaks of the spectra recorded at various spectrometer frequencies. The spectrum of compound II recorded at 24.24 MHz clearly shows an AB NMR pattern for the ^{31}P resonances of the two different triphenylphosphine ligands. But at 121.49 MHz frequencies the near AX NMR pattern may be obtained. The values of $\delta(P^2)$ and $\delta(P^1)$ were calculated from the experimental data taking into account the position of the $CpRuCl(PPh_3)_2$ signal which served as internal reference. The coupling constant $J(P^1RuP^2)$ is almost unaffected by the nature of the X anion (Table 1).

The doublet centered in the region at about δ(37.7–37.3) ppm corresponds to the P^1 phosphorus atom and its position depends only slightly on the nature of the solvent and X anion. But the second doublet centered in the range δ(42.8–41.9)



Scheme 2

ppm corresponding to the P^2 phosphorus atom clearly depends on the environment of the $Cp^2Ru(\eta^6\text{-}C_6H_5)P^2Ph_2$ moiety. This assignment is generally based on the values of the chemical shifts of the $\delta(CpRuCl(PPh_3)_2)$ (δ 38.34 ppm in chloroform) and $\delta([CpRu(CO)(PPh_3)_2]BPh_4)$ (δ 41.45 ppm in chloroform) [3] which are closer to the $\delta(P^1)$ and $\delta(P^2)$ values. In particular, the effect of chloride anion in compound VI on the upfield shift of P^2 phosphorus atom, compared with that of compound II containing tetraphenylborate anion, is significant and suggests that compound VI has significantly covalent $Ru^+\text{---}Cl^-$ bond, Scheme 3.



Compound VI

Scheme 3

Table 1

The effect of the nature the of solvent and the type of anion in compounds II and VI on the $\delta(P^2)$ and $\delta(P^1)$ chemical shifts in the ^{31}P NMR data.

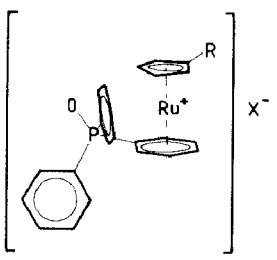
Solvent	$CpRuCl(PPh_3)_2$ (ppm)	Compound	$\delta(P^2)$ (ppm)	$\delta(P^1)$ (ppm)	$J(P^1RuP^2)$ (Hz)
$CHCl_3$	38.34	II	42.37	37.67	42.9
		VI	41.94	37.53	42.2
CH_2Cl_2	38.40	II	42.75	37.43	43.4
		VI	42.00	37.33	42.8
Pyridine	38.95	II	42.82	37.57	42.6
		VI	42.15	37.72	42.4

The expected and the observed effects of the increased electron density on the ruthenium atom π-bonded to the phenyl ring from PPh_3 molecule, as well as on the upfield shift of P^2 atom in ^{31}P NMR spectrum are presented in Table 1. Whereas the P^2 atom clearly shifts upfield in accordance with the rule given previously [2], the P^1 phosphorus atom is shifted only weakly; in general the changes lie within experimental error. Owing to the large separation, the influence of the Cl^- anion on the P^1 atom is weak.

Similar behaviour was observed in ^1H NMR studies of compounds II and VI (Experimental i). The position of the Cp^1 ring is fixed, and at the same position of the Cp in $CpRuCl(PPh_3)_2$ (δ 4.01 ppm). The position of the Cp^2 ring depends on the nature of the solvent used to prepare the sample solution in the NMR tube and especially on the type of X anion. For compound II as the chloroform solvate ($II \cdot CHCl_3$) dissolved in deuterated pyridine the resonance of the Cp^2 ring is shifted to significantly lower fields (δ 4.61 (s) ppm) than the non-solvated II (δ 4.35 ppm), (Experimental i). In order to obtain good spectra in $CDCl_3$ the sample solution must be left to stand in the NMR tube during a few hours before the ^1H NMR measurement. This can be explained by either the reorientation mechanism of the ion-pair proceeding by several conformational stages, each connected by a slow change of ligand positions or by the orientation in the complex, of the bonded solvate molecule.

The ^1H NMR($CDCl_3$) spectrum of compound VI shows the fixed position of Cp^1 (δ 4.03 ppm) and downfield position of Cp^2 (δ 4.76 ppm), shifted because of the chloride anion interaction, Scheme 3. This downfield shift of Cp^2 ring resonance implies increased electron density at the ruthenium atom which leads to increased paramagnetic shielding of the Cp^2 protons [14]. This indicates that either the aromatic solvent (pyridine) or the type of anion present in the ion-pairs (halogenide in place of BPh_4^- anion) plays a role similar to that of the complex having potential as NMR shift reagent for the cyclopentadienyl ring protons. The rather similar conclusions were drawn from the NMR data for the compounds XI–XIV because they resemble those of the fragments of the extended compounds I–VIII.

The crystal structure of the above cation has been elucidated by Oro and coworkers who examined the ion-pair with perchlorate anion [15]. A precise structure of the $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]^+$ cation deduced from published X-ray data is depicted in Fig. 1. It is very probable that in compounds I–VIII the relevant fragment is similar to $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]^+$, the structure given by Oro et al. with replacement of the oxygen atom by ruthenium atom.



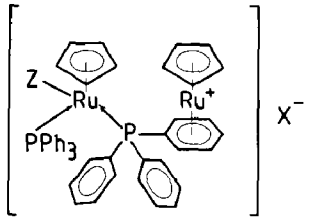
	R	X
XI	H	BPh_4
XII	CH_3	BPh_4
XIII	H	Cl
XIV	CH_3	Cl

Fig. 1.

For the non-methylated compounds XI and XIII the replacement of tetraphenylborate anion by chloride anion also causes the marked downfield shift of the Cp proton signals, from δ 4.72 ppm to δ 5.37 ppm (as can be seen from proton NMR ($CDCl_3$) spectra of compounds XI and XIII). Similar effects have been observed in the proton NMR spectrum of compound XI, δ(Cp) 5.10 ppm, (Experimental iv), recorded in pyridine solution.

MS(FD) investigations

The MS(FD) studies of compounds II and VI showed the signals centered at *m/e* 893 to be the main signals.



	Z	X
XV	Br	Br
XVI	Br	BPh_4
XVII	I	I
XVIII	I	BPh_4

The use of $CpRuBr(PPh_3)_2$ or $CpRuI(PPh_3)_2$ as a substrate in either the high-temperature method (reflux in ethylene glycol, Experimental i) or in the low-temperature method, gives the expected compounds XV–XVIII. Signals were found at *m/e* 937 (for compounds XV and XVI) and at *m/e* 985 for compounds XVII and XVIII, respectively, as expected from calculations and the computer simulation for the extended cations studied.

When a mixture of $CpRuCl(PPh_3)_2$ and its methyl derivative (η^5-$C_5H_4CH_3$)$RuCl(PPh_3)_2$ is used as substrate to prepare the methyl analogues of compound II (as described in Experimental i), the mixture of compounds I–IV that results gives three groups of MS(FD) signals centered at *m/e*: 893, non-methylated cation from compound II; 907, mono-methylated cations (compounds I, IV) and 921, di-methylated cation from compound III. This result is consistent with the expectations associated with the presence of two cyclopentadienyl rings in our extended cations, (Formulas 1).

^{31}P NMR investigations

Recently during the phosphorus NMR studies investigations of the compounds I–IV (or V–VIII) the presence of four different compounds connected with partition of the methyl substituent at Cp rings has been confirmed. The phosphorus NMR data for these compounds are listed in Table 2. The tetraphenylborates (compounds I–IV), examined either in chloroform or pyridine solutions, comply exactly with the rule stated previously [2] about the shifts of the phosphorus atom from triphenylphosphine in ^{31}P NMR spectra caused by the introduction of the methyl group into the cyclopentadienyl rings.

Thus, the rule may be presented as follows: *if bonding of the ruthenium atom with the triphenylphosphine ligand is by free electron pairs on the phosphorus atom (PPh_3 acts as σ-donor ligand) then the introduction of a methyl group into the Cp-ring causes a downfield shift of the phosphorus atom signal.* When the ruthenium atom is

Table 2

The effect of the methyl substituent in the dinuclear compounds I–VIII on chemical shifts observed in the ^{31}P NMR data recorded on a Bruker 121.49 MHz spectrometer, δ (ppm).

Compound	$\delta(P^2)$	Shifts [a]	$\delta(P^1)$	Shifts [a]
In chloroform:				
I	42.21		37.65	
II	42.35	L	37.67	L
III	43.80	L	38.69	L
IV	43.90	L	38.70	L
V	42.00		37.47	
VI	41.85	R	37.47	N
VII	43.50	L	38.19	L
VIII	43.40	R	38.45	L
In pyridine:				
I	42.78		37.48	
II	42.93	L	37.57	L
III	44.15	L	38.38	L
IV	44.28	L	38.48	L
V	42.15		37.66	
VI	42.15	N	37.70	L
VII	43.49	L	38.56	L
VIII	43.43	R	38.62	L

[a] L = shift to left, R = shift to right, N = no shift.

π-bonded to phenyl ring of PPh_3 ligand, the introduction of a methyl group into the Cp-ring gives an upfield shift of phosphorus atom signal in ^{31}P NMR spectrum [2]. In the case of π-bonded phenyl ring system (to ruthenium atom) it is well known that bonding of this kind produces shifts of the proton resonances to higher fields because of factors such as the withdrawal of π-electron density from the phenyl ring by the ruthenium [17].

This phenomenon is extended to the effect of methyl substitution at Cp-ring and to the changes observed in the phosphorus NMR spectrum. The compounds given in Table 2 are arranged such a way that the next compound (from II up to IV or from VI up to VIII) must be shifted to the left in accordance with the presented rule.

The use of a mixture of $CpRuCl(PPh_3)_2$ and its methyl derivative as substrate and depending on the molar ratio methylated/non-methylated of the mixture various product mixtures can be obtained, for example, only the compounds I and II mixture, Experimental iii. Compounds III and IV were not-detected in the post-reaction mixture. The effect of the methyl group introduced into the Cp-ring, which facilitates the formation of the ruthenium π-bond with the phenyl ring, can clearly be seen. Thus, the most likely methylated product is compound I having the methyl-substituted Cp-ring at ruthenium π-bonded to the phenyl ring of one of the two PPh_3 ligands.

When X = Cl (compounds V–VIII), some deviations from the rule are noted, Table 2, probably because of the significantly covalent character of the Ru^+---Cl^- bond which masks the effect by the methyl substituent in the Cp^2 ring (Scheme 3). The deviation from the rule is not observed for the P^1 phosphorus atom σ-bonded to

Table 3

The effect of the methyl substituent in the Cp-ring on the shifts of the phosphorus signal in ^{31}P NMR spectra of compounds containing π-bonded triphenylphospine ligand (compounds IX–X) and triphenylphosphine oxide ligand (compounds XI–XIV).

Compounds	δ(ppm) all singlets		
	R = H	R = CH_3	Free ligand
In chloroform			
IX–X	−5.65	−7.71	
PPh_3			−5.64
XI–XII	25.44	25.60	
XIII–XIV	25.25	25.35	
$Ph_3P{=}O$			28.51
In pyridine			
IX–X	−5.49	−6.97	
PPh_3			−5.37
XI–XII	24.12	24.21	
XIII–XIV	23.70	23.72	

ruthenium atom, although ruthenium is also connected to the chlorine atom and the Cp^1 ring.

When the phosphorus atom (originating from the triphenylphosphine molecule π-bonding the phenyl ring to the ruthenium atom) reduces the electron density, the methyl substituent effect disappears or can even be reversed. The last phenomenon was observed for compounds containing the triphenylphosphine oxide molecule π-bonded to ruthenium by phenyl ring, compounds XI–XIV, Table 3. The electronegativity of substituents on phosphorus is one of the most important variables determining chemical shifts [18] and the signal is shifted to higher fields, owing to a change in the ruthenium induced by oxygen, at about 43 ppm compared with about 25 ppm for compounds XI–XIV. Little or no change is caused by introduction of a methyl group into the Cp-ring for compounds containing triphenylphosphine oxide ligand (compounds XI–XIV); the relevant data lie within experimental error.

But the reduction of the electron density at phosphorus atom, mentioned above, is not only reason for the deviation from the rule, because compounds I–VIII, in their ^{31}P NMR spectra show signals lying at an even greater distance downfield than that mentioned. Further studies should also take into account the magnetic anisotropy of the P=O bond (interatomic distance 1.486 Å [15]).

The rule presented is manifested only in the expected and observed increase in the distance between carbon atom of the phenyl ring π-bonded to the phosphorus atom (C–P 1.821 Å) compared with the two remaining C–P distances (1.803 and 1.802 Å) as can be seen from the X-ray data [15]. This is a final result of the influence of back-donation of electrons of the ruthenium atom to the arene ligand [2].

Conclusions

Formation of dinuclear complexes such as compounds I–VIII also proceeds during reflux of the compounds, $CpRuCl(PPh_3)_2$ in lowboiling alcohols (methanol,

ethanol) in contact with oxygen [3]. From the published data it is known that $CpRuCl(PPh_3)_2$ in methanol in a Carius tube at 85 °C for several hours is recovered unchanged [19]. However, it has been suggested by a number of workers that $CpRuCl(PPh_3)_2$ in methanol solution undergoes dissociation [9,20–24]:

$$CpRuCl(PPh_3)_2 + MeOH \rightleftarrows [CpRu(MeOH)(PPh_3)_2]^+ + Cl^- \quad (1)$$

The solvated cation probably exists only in equilibrium (1) [20] and attempts to isolate as the ion-pair with tetraphenylborate anion, and to characterize it, have met with little success [21].

The experimental data do raise some points:

i. The first stage is the dissolution of $CpRuCl(PPh_3)_2$ to form the $[CpRu(solv)(PPh_3)_2]^+$ cation (solv=MeOH,EtOH), which is in equilibrium with the $CpRuCl(PPh_3)_2$. The solvent molecule is exceptionally labile towards replacement [20].

ii. The presence of traces of oxygen causes the formation mainly of $Ph_3P{=}O$ (for solv = MeOH) or $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]Cl$ (compound XIII, for solv = EtOH) and simultaneously the formation of a dinuclear cation (compound VI). The molar ratio of the total phosphorus content in $Ph_3P{=}O$ and $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]Cl$ to that in the dinuclear cation is almost 1. In all cases significant amounts of unchanged $CpRuCl(PPh_3)_2$ were recovered. Traces of PPh_3 are present only when solv = EtOH. Thus, the formation of dinuclear cation (compound VI) is closely associated with the simultaneous formation of $Ph_3P{=}O$.

iii. One PPh_3 molecule most probably dissociates from the crowded solvated cation:

$$[CpRu(solv)(PPh_3)_2]Cl \rightarrow CpRuCl(solv)PPh_3 + PPh_3 \quad (2)$$

The labile, intermediate species $CpRuCl(solv)PPh_3$ postulated, having σ-bonded PPh_3 molecule, readily undergoes reaction with $NaBPh_4$ solution to give the ion-pair (compound IX) containing the now π-bonded PPh_3 molecule:

$$CpRuCl(solv)PPh_3 + NaBPh_4 \rightarrow [CpRu(\eta^6\text{-}C_6H_5)PPh_2]BPh_4 + solv + NaCl \quad (3)$$

Experimental data confirm this since the ^{31}P NMR spectrum of the evaporated ethanolic post-reaction solution gave only the PPh_3 signal in the negative range of chemical shift scale (δ −5.37 ppm, insignificant). The isolated sparingly soluble tetraphenylborates gave signals at δ −5.49 ppm (compound IX) and δ −6.97 ppm (methylated compound X, for the methylated/non-methylated substrate mixture, Table 3) and traces of PPh_3 δ −5.37 ppm. This phenomenon has previously been observed for solv = ethylene glycol; the signal at δ 32 ppm in the phosphorus NMR spectrum may be assigned to the σ-bonded PPh_3 complex [1].

iv. The mechanism by which oxygen acts is not clear as yet and may be similar to that postulated by Bruce and coworkers [23]. The solvent molecule can be displaced by molecular oxygen to give the oxo-intermediate species, which in turn undergoes an intramolecular oxygen transfer to phosphorus. Thus, following pathways are possible:

$$[CpRu(solv)(PPh_3)_2]^+ + O_2 \rightarrow [CpRu(O_2)(PPh_3)_2]^+ + solv \quad (4)$$

$$[CpRu(O_2)(PPh_3)_2]^+ \rightarrow CpRu^+ + 2Ph_3P{=}O \quad (5)$$

$$CpRuCl(PPh_3)_2 + CpRu^+ \rightarrow [CpRuCl(PPh_3)CpRu(\eta^6\text{-}C_6H_5)PPh_2]^+ \quad (6)$$

This can account for the formation during reflux in MeOH of two moles of $Ph_3P{=}O$

against 1 mole of dinuclear compound VI, Experimental ii.

v. A larger volume of oxygen (air) bubbled through the reaction mixture causes further formation of free triphenylphosphine oxide and decreased amounts of the dinuclear cation (compound VI), are observed. The maximum yield of [CpRu(η^6-C_6H_5)Ph_2P=O]BPh_4 (compound XI) was only 50%, Experimental iv.

Thus the maximum yield of dinuclear cation (in compounds II or VI) cannot exceed 50%, in practice 30–40% is acheived. Oxygen plays the role of labilizing agent to the PPh_3 ligands in the $CpRuCl(PPh_3)_2$ substrate which facilitates the dissociation process (5). In the case of high-boiling solvents such as ethylene glycol, the presence of oxygen is not necessary for dissociation process to occur.

Experimental

General experimental conditions and apparatus are similar to those described in previous parts of this series (see ref. 16). Proton-noise decoupled ^{31}P NMR spectra were recorded at 24.24 MHz on a JEOL JNM-FX60 spectrometer, as well as at 36.43 MHz and at 121.49 MHz on a Bruker HFX72 spectrometer. The MS(EI) spectra were recorded with an LKB BROMMA 2091 mass spectrometer at variable ionizing voltage (up to 70 V) and on a JEOL JMS-D100 at an ionizing voltage of 75 V. The proton NMR spectrometers were operated at 60, 80 and 100 MHz(FT).

i. Preparation of $[Cp^1RuCl(P^1Ph_3)Cp^2Ru(\eta^6\text{-}C_6H_5)P^2Ph_2]BPh_4 \cdot CHCl_3$ *(II* $\cdot$ $CHCl_3$*), high-temperature method.* A typical preparation very similar to that described previously [1] was used. 1.0258 g of powdered $CpRuCl(PPh_3)_2$ and 75 cm^3 of ethylene glycol were refluxed for 1 min, measurement of the reflux time was commenced once the ethylene glycol began to boil. After rapid cooling to room temperature 150 cm^3 of MeOH were added and the mixture was left to stand for 3 d. The precipitated $CpRuCl(PPh_3)_2$ substrate was filtered off (0.3596 g, 35% of recovery). To the clear filtrate was added a solution of 0.6 g of sodium tetraphenylborate in 10 cm^3 of MeOH. The yellow precipitate was filtered after one day of storage to give a mixture of compounds II and IX (0.3538 g). Then the mixture was washed with 4 cm^3 of chloroform, to give the insoluble white precipitate, [CpRu(η^6-C_6H_5)PPh_2]BPh_4 (compound IX, 0.1486 g, m.p. 196-214°C, 14% yield). The filtrate was evaporated to dryness to give 0.2273 g of golden-yellow flakes (compound II $\cdot$ $CHCl_3$) in 24% yield. Anal. Found: C 64.2, Cl 8.6. $C_{71}H_{61}BP_2Cl_4Ru_2$ calc: C 64.0, Cl 10.6%. ^1H NMR: $\delta(CDCl_3)$ 4.03 (s,5H,Cp^1), 4.26 (s,5H,Cp^2); ^1H NMR δ(pyridine-d_5) 4.00 (s,5H,Cp^1), 4.61 (s,5H,Cp^2); MS(FD) *m/e* 893 (parent ion of the complex cation).

But after recrystallization of the solvate II $\cdot$ $CHCl_3$ by dissolution in diglyme and inducing precipitation with a few drops of methanol, the yellow compound II, m.p. 178–187°C, was obtained [1] which gives a different location of Cp^2 protons resonances in its ^1H NMR spectra. ^1H NMR: $\delta(CDCl_3)$ 4.03 (s,5H,Cp^1), 4.31 (s,5H,Cp^2); ^1H NMR: δ(pyridine-d_5) 4.02 (s,5H,Cp^1), 4.35 (s,5H,Cp^2). Compound II after recrystallization is not solvated.

ii. Preparation of compound VI by reflux of $CpRuCl(PPh_3)_2$ *in methanol (low-temperature method).* 0.3169 g of $CpRuCl(PPh_3)_2$ and 200 cm^3 of MeOH were refluxed for 0.5 h. Refluxing system was not protected against air access. After cooling and filtration (0.0501 g of unchanged $CpRuCl(PPh_3)_2$ was filtered off, 16% recovery) the yellow solution was evaporated to dryness, to give 0.2780 g of a

yellow, vitreous substance which was found to contain: compound VI (40%), triphenylphospine oxide (37%), compound XIII (4%) and unchanged $CpRuCl(PPh_3)_2$ (19%). The proportions were calculated relative to the amounts of phosphorus present and the data were taken from phosphorus NMR spectrum of a 0.2780 g sample.

iii. Preparation of the mixture containing compounds I and II. 0.4662 g of mixture containing 75% mol. $CpRuCl(PPh_3)_2$ and 25% mol. $(\eta^5\text{-}C_5H_4CH_3)RuCl(PPh_3)_2$ and 100 cm^3 of EtOH were refluxed for 2 h and left to stand for 7 d of storage. After filtration (0.1367 g, 29% recovery of the substrate mixture), to the clear filtrate was added 0.3 g of $NaBPh_4$ in 7 cm^3 of EtOH and after 5 min a yellow precipitate formed. 0.0438 g of a mixture containing compound I (1.6% yield), compound II (2.8% yield) and compounds XI and XII (1.8% yield) were obtained.

iv. Preparation of $[CpRu(\eta^6\text{-}C_6H_5)Ph_2P{=}O]BPh_4$*, compound XI.* 0.2704 g of $CpRuCl(PPh_3)_2$ and 50 cm^3 of MeOH were refluxed for 3 hours, during which air was bubbled through at intervals to give a pale-yellow solution, which was evaporated to dryness and left to stand for 3 days. Then 50 cm^3 of MeOH were added, the mixture was filtered, and to the filtrate was added 0.1 g of $NaBPh_4$ in 5 cm^3 of MeOH to form a suspension which was filtered off after 5 minutes (0.0234 g, contaminated compound XI, 8% yield). The filtrate was left to stand for 2 days, and the white, needle-shaped crystalline compound was filtered, to give 0.1163 g of pure compound XI, in 41% yield. ^1H NMR: $\delta(CDCl_3$, FT 120 scans) 4.72 (s,5H,Cp), 5.69 and 5.12 (m,5H,$\eta^6\text{-}C_6H_5$), 7.64, 7.43 and 6.92 (m,30H,$Ph_2 + BPh_4$); ^1H NMR: δ(pyridine-d_5) 5.10 (s,5H,Cp), 6.40 and 6.04 (m,5H,$\eta^6\text{-}C_6H_5$), 7.91, 7.48 and 7.12 (m,30H,$Ph_2 + BPh_4$); ^{31}P NMR: δ(pyridine) 24.12 (s,$Ph_3P{=}O$); ^{11}B NMR: δ(DMSO-d_6) -1.65 (s,BPh_4). MS(FD) *m/e* 445; IR(KBr) 3048m, 2976w, 1558m, 1460s, 1421s, 1410w, 1383w, 1300w, 1265m, 1200vs, 1117vs, 1062m, 1032w, 1010w, 850s, 751m, 740s, 712vs, 610s, 534vs, 435m.

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