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Cyclopentadienyl-ruthenium and -osmium complexes

VII *. Formation and properties of ion-pairs containing the dihydride(η-cyclopentadienyl)bis(triphenylphosphine)-ruthenium(IV) cation

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Abstract

The $[CpRuH_2(PPh_3)_2]^+$ cation in the simple and fast reaction of $CpRuH(PPh_3)_2$ with organic sulphonic acids in polar solvents (methanol, acetone) has been obtained in the form of ion-pairs. The reaction runs for several minutes, with practically quantitative yields. The dihydride complex cation obtained may be isolated from polar solutions as a sparingly soluble ion-pair $[CpRuH_2(PPh_3)_2][BPh_4]$ with the tetraphenylborate anion.

In the $[CpRuH_2(PPh_3)_2]$[sulphonate] ion-pairs a reduction–elimination process slowly proceeds with the formation of non-ionic compounds of the CpRu(sulphonate)$(PPh_3)_2$ type. Also, the effect of methyl substituents in the Cp-ring on shifts in the ^{31}P NMR signals and MS(FD) investigations of the new compounds obtained have been described. Explanation of the new group signals in the MS(FD) spectra as originating from the fragments formed, containing two ruthenium atoms π-bonded to the phenyl ring of BPh_4, i.e. $[CpRu(\eta^6\text{-}C_6H_5)BPh_2CpRu(\eta^6\text{-}C_6H_5)]^+$, were proposed. In the case of compounds containing the PPh_3 molecule, a similar phenomenon occurs. For fragments obtained in the MS(FD) spectra, the formula $[RSO_3CpRuPPh_2CpRu(\eta^6\text{-}C_6H_5)]^+$ was ascribed.

Introduction

Since 1981 it has been known [1] that $CpRuH(PPh_3)_2$, discovered in 1971 by Blackmore, Bruce and Stone, undergoes a reaction in polar media with halogenohydro acids HX, giving halogeno(η-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) $CpRuX(PPh_3)_2$, in high yield.

* For Part VI see Ref. 5.

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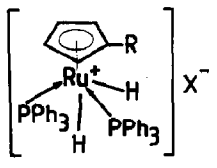
Bruce [2] was the first to obtain the complex cation $[CpRuH_2(PPh_3)_2]^+$. In 1983 Bruce obtained this cation in the reaction of $CpRuH(PPh_3)_2$ with a strong organic acid, pentakis(methoxycarbonylcyclopentadiene), $HC_5(CO_2Me)_5$ [3], in the state of a colourless salt $[CpRuH_2(PPh_3)_2][C_5(CO_2Me)_5]$. Unfortunately, the above-mentioned ion-pair (salt) obtained is insoluble in most common solvents. It dissolves rapidly in chlorinated solvents to give $CpRuCl(PPh_3)_2$.

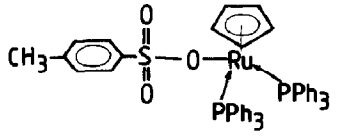
Also, Simpson and Conroy-Lewis [4] obtained the dihydride cation $[CpRuH_2(Ph_2PCH_2CH_2CH_2PPh_2)]^+$ by treatment of $CpRuH(Ph_2PCH_2CH_2CH_2PPh_2)$ with HPF_6. This cation exhibits a triplet in the ^1H NMR spectrum ($\delta - 8.62$ t, J (PH) 28 Hz). It is of interest that protonation of ruthenium hydride containing the smaller chelating diphosphine gave the molecular dihydrogen cation $[CpRu(\eta^2\text{-}H_2)(Ph_2PCH_2PPh_2)]^+$. This cation shows a broad signal at $\delta - 6.98$ ppm in the ^1H NMR spectrum.

At present, it appears that in the reaction of $CpRuH(PPh_3)_2$ with organic sulphonic acids, the ion-pairs $[CpRuH_2(PPh_3)_2]^-$ [sulphonate] are also formed. The reaction is fast in polar media (methanol), lasting only several minutes, and gives a practically quantitative yield. In the above oxidation–addition reaction, a change in the oxidation state of ruthenium to ruthenium(IV) is formally required.

Results and discussion

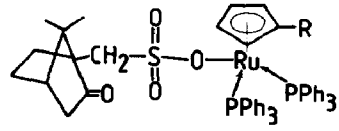
The reaction of $CpRuH(PPh_3)_2$ with organic sulphonic acids runs in parallel to that of osmium hydride $CpOsH(PPh_3)_2$ [5]. It is possible that the reaction of $CpRuH(PPh_3)_2$ with HX acids forms intermediate $[CpRuH_2(PPh_3)_2]X$ ion-pairs, which in the very fast reduction–elimination process give the covalent $CpRuX(PPh_3)_2$. Thus, in the case of ruthenium the main product is covalent $CpRuX(PPh_3)_2$, while in the case of $CpOsH(PPh_3)_2$ the product is a $[CpOsH_2(PPh_3)_2]X$ ion-pair.





(VII)

	R	X
I	H	p-toluenesulphonate
II	H	d(+)campho-10-sulphonate
III	CH_3	p-toluenesulphonate
IV	CH_3	d(+)campho-10-sulphonate
V	H	BPh_4
VI	CH_3	BPh_4



	R
VIII	H
IX	CH_3

Table 1

Yields, melting points and mass spectral data for the new compounds

Compound	MS(FD) parent ion m/e [a]	Mol. wt. (calcd.)	Colour	M.p. (°C)	Yield (%)	Substrate used for synthesis
$[CpRuH_2(PPh_3)_2]$-$[SO_3C_6H_4CH_3]$ (I)	[b]	863.9	yellow		100	$CpRuH(PPh_3)_2$
$[CpRuH_2(PPh_3)_2]$-$[SO_3C_{10}H_{15}O]$ (II)	[b]	924.0	yellow		100	$CpRuH(PPh_3)_2$
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2]$-$[SO_3C_6H_4CH_3]$ (III)	[b]	878.0	yellow		100	$(\eta\text{-}C_5H_4CH_3)$-$RuH(PPh_3)_2$
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2]$-$[SO_3C_{10}H_{15}O]$ (IV)	[b]	938.0	yellow		100	$(\eta\text{-}C_5H_4CH_3)$-$RuH(PPh_3)_2$
$[CpRuH_2(PPh_3)_2][BPh_4]$ (V)	691 [c] (−2H)	1012.0	white--yellow	147–150 dec	89	compound II
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2]$-$[BPH_4]$ (VI)	707 [c]	1026.0	white--yellow		88	compound IV
$CpRuOSO_2C_6H_4CH_3(PPh_3)_2$ (VII)	862	861.9	yellow	197–205	25	compound I
$CpRuOSO_2C_{10}H_{15}O(PPh_3)_2$ (VIII)	922	922.0	yellow--orange	218–238	32	compound II
$(\eta\text{-}C_5H_4CH_3)RuOSO_2C_{10}H_{15}O$ $(PPh_3)_2$ (IX)	936	936.0	yellow--orange		18	compound IV

[a] Data for ^{102}Ru, ^{11}B and ^{32}S isotopes. [b] Impossible to obtain in the solid state. [c] The dissociation of the compound to complex cation.

In contrast to Bruce's $[CpRuH_2(PPh_3)_2][C_5(CO_2Me)_5]$ ion-pair [2], the $[CpRuH_2(PPh_3)_2]$[sulphonate] ion-pair obtained in the reaction of $CpRuH(PPh_3)_2$ with organic sulphonic acids is very soluble in polar media. The reaction is fast, despite the heterogeneous reaction conditions (solid phase of the $CpRuH(PPh_3)_2$). The solution obtained contains practically only the $[CpRuH_2(PPh_3)_2]^+$ cation, which decreases in amount during storage, as seen from the NMR spectra. In ^1H NMR spectra, the triplet δ(Ru–H) at −7.2 ppm can be seen. Integration of the δ(Ru–H) triplet intensity in the spectra compared with the intensity of the Cp-ring singlet gives values of about two protons. As can be seen from the proton-decoupled ^{31}P NMR spectra, the location of the expected PPh_3 singlet at about 57 ppm from two equivalent phosphorus atoms is almost independent of the kind of X^- anion.

The $[CpRuH_2(PPh_3)_2]^+$ cation can easily be isolated as sparingly soluble ion-pairs with a small excess of tetraphenylborate anion from solution in polar solvents in a yield of about 90%. The ion-pairs obtained with tetraphenylborate anion are stable in the solid state and soluble in most solvents (Tables 1 and 2). In the IR(KBr) spectra of $[CpRuH_2(PPh_3)_2][BPh_4]$ there are two very weak bands at about 2070 and 2050 cm^{-1}, showing antisymmetric and symmetric ν(Ru–H) vibrations. Regarding the probable *trans*-configuration of the hydrogen atoms in the $[CpRuH_2(PPh_3)_2]^+$ cation, a diagonal configuration in accordance with Bruce is proposed [6]. Although compounds V and VI obtained in chlorinated solvents (e.g. $CHCl_3$) slowly transform into covalent $CpRuCl(PPh_3)_2$ compounds during storage at room temperature, NMR investigations in chlorinated solvents are possible.

Similarly, when to a solution of the ion-pair $[CpRuH_2(PPh_3)_2]$[sulphonate] the X^- anion is added (X = Cl, Br), covalent $CpRuX(PPh_3)_2$ can also be obtained (see

Table 2

NMR data of the new cyclopentadienylruthenium complexes (chemical shifts in ppm, δ)

Compound	^{1}H NMR (TMS)				Others	^{31}P NMR(H_3PO_4)	
	Solvent	Cp	PPh_3	Ru–H, J (PH) (Hz)		Solvent	PPh_3
$[CpRuH_2(PPh_3)_2][SO_3C_6H_4CH_3]$ (I)	CD_3OD	4.93 s	7.30 m	not observed [a]	C_6H_4 7.67d, 7.10d,J(HH) 8 Hz; CH_3 2.30 s	MeOH	57.1s
	CH_3OH			−7.24t 24			
$[CpRuH_2(PPh_3)_2][SO_3C_{10}H_{15}O]$ (II)	CD_3OD	4.99s	7.34m	not observed [a]	$C_{10}H_{15}O$ 3.5–0.6m	MeOH	57.3s
	CH_3OH			−7.23t 24			
	$(CD_3)_2SO$	5.05s	7.32m	−7.26t 24	$C_{10}H_{15}O$ 3.5–0.6m		
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2][SO_3C_6H_4CH_3]$ (III)	CD_3OD	4.98s, 4.63s, 1.40s	7.32m	not observed [a]	C_6H_4 7.70d, 7.23d, J(HH) 8 Hz; CH_3 2.30s	MeOH	58.5s
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2][SO_3C_{10}H_{15}O]$ (IV)	CD_3OD	4.98s, 4.63s, 1.40s	7.30m	not observed	$C_{10}H_{15}O$ 3.5–0.6m	MeOH	58.6s
	CH_3OH			−7.26t 24			
$[CpRuH_2(PPh_3)_2][BPh_4]$ (V)	$CDCl_3$	4.50s	7.14m	−7.44t 24	BPh_4 6.86m, 6.75m	$CHCl_3$	58.1s
$[(\eta\text{-}C_5H_4CH_3)RuH_2(PPh_3)_2][BPh_4]$ (VI)	$CDCl_3$	4.48s, 4.21s, 1.30s	7.13m	−7.52t 24	BPh_4 6.86m, 6.76m	$CHCl_3$	59.4s
$CpRuOSO_2C_6H_4CH_3(PPh_3)_2$ (VII)	$CDCl_3$	4.27s	7.07m		CH_3 2.23s	Benzene	40.0s
$CpRuOSO_2C_{10}H_{15}O(PPh_3)_2$ (VIII)	$CDCl_3$	4.35s	7.18m		$C_{10}H_{15}O$ 3.5–0.6m	Benzene	40.68d 40.11d
						$J(P^1RuP^2)$	40 Hz
						$CHCl_3$	40.0s

[a] After several minutes of storage of the sample solution a weak triplet at δ −7.26 ppm, J(PH) 24 Hz, is observed.

Table 3

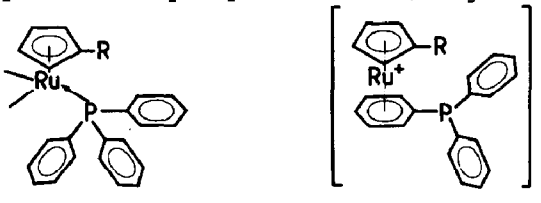
The effect of the methyl group on $\delta(PPh_3)$ shifts in the $^{31}P\{^1H\}$ NMR investigations

Compound	^{31}P NMR δ (H_3PO_4)			Ref.	Shifts
	Solvent	R = H	$R = CH_3$		
$[(C_5H_4R)RuH_2(PPh_3)_2]$ [*p*-toluenesulphonate]	MeOH	57.1s	58.5s	This work	←
$[(C_5H_4R)RuH_2(PPh_3)_2]$ [*d*(+)campho-10-sulphonate]	MeOH	57.3s	58.6s		←
$[(C_5H_4R)RuH_2(PPh_3)_2]$ $[BPh_4]$	$CHCl_3$	58.1s	59.4s		←
$[(C_5H_4R)Ru(CO)(PPh_3)_2]$ $[BPh_4]$	CH_2Cl_2	41.2s	41.9s	[7]	←
$(C_5H_4R)RuCl(PPh_3)_2$	$CHCl_3$	39.5s	40.8s	[8]	←
$(C_5H_4R)RuOSO_2C_{10}H_{15}O(PPh_3)_2$ (VIII and IX)	Benzene	40.68d	40.78d		
		40.11d	40.05d		
		$J(P^1RuP^2)$	40 Hz	This work	←
Compounds XII and XIII, $R = R^2$	Pyridine [a]	42.4d	42.0d		
		37.2d	36.5d		→
Compounds XIII and XIV, $R = R^1$	Pyridine [a]	42.0d	43.4d		
		36.5d	37.4d		
		$J(P^1RuP^2)$	43 Hz	[7,8]	←
$[(C_5H_4R)Ru(\eta^6\text{-}C_6H_5)PPh_2][BPh_4]$ (X and XI)	Pyridine	−6.1s	−7.7s	[7]	→

[a] Spectra were made on a ^{31}P NMR Jeol JNM-FX60 (24.2 MHz) apparatus. $CpRuCl(PPh_3)_2$ resonates at 38.4 ppm.

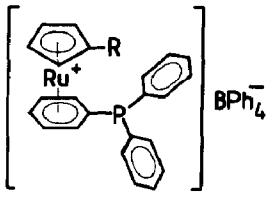
Experimental *x*). A similar phenomenon was observed in the osmium analogue [5], but the yield of $CpRuX(PPh_3)_2$ is higher than in the osmium case. The above-mentioned reactions of the reduction–elimination process occur also in the case of pure $[CpRuH_2(PPh_3)_2][sulphonate]$ solutions, without any foreign ions (e.g. Cl^-, Br^-). During storage of these ion-pairs a reduction–elimination process occurs, finally giving new covalent compounds VII–IX. In the case of the osmium analogue [5] in the MS(FD) spectra of the $[CpOsH_2(PPh_3)_2][sulphonate]$ ion-pair compound, only *m/e* values of 1012 and 952 for the covalent compound with the rest of the *d*(+)campho-10-sulphonic acid and *p*-toluenesulphonic acid, as a result of rearrangement on the emitter MS device, were found. Thus, at present, there is full analogy in the reaction for ruthenium and osmium hydride with acids.

Introduction of a methyl group into the Cp-ring causes changes in the ^{31}P NMR (Table 3) and IR spectra (in the case where the C≡O molecule is present as ligand). If bonding of the ruthenium atom with the PPh_3 molecule is made by free electron pairs of the phosphorus atom (PPh_3 acts as δ-donor ligand, Scheme 1a), then a

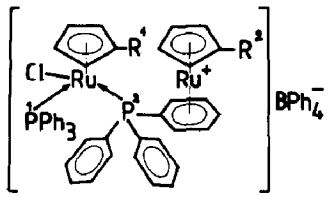


a b

Scheme 1



	R
X	H
XI	CH_3



	R^1	R^2
XII	H	H
XIII	H	CH_3
XIV	CH_3	CH_3

significant shift downfield from the free ligand in the ^{31}P NMR spectra is observed. The introduction of a methyl group into the Cp-ring also causes a shift downfield, but only slightly (shift to the left). If bonding of the ruthenium atom with the PPh_3 molecule is made by participation of the π-electrons of the phenyl ring of PPh_3 (X–XIV, Scheme 1b, Table 3), then a small upfield shift is observed ($\delta - 6.1$ ppm for compound X, in comparison with $\delta - 6.0$ ppm for free PPh_3). The one phenyl ring of PPh_3 acts as a δ-donor/π-acceptor ligand. Introduction of a methyl group into the Cp-ring causes a significant upfield shift: compound XI, $\delta - 7.7$ ppm (shift to the right).

In both cases, the introduction of a methyl group into the Cp-ring causes an increase in the electron density on the ruthenium atom. Consequently, the participation of back-bonding from ruthenium to the phenyl ring (or the other ligand being a δ-donor/π-acceptor, e.g. C≡O) is increased.

Carbon monoxide as a ligand is a good indicator of back-bonding participation. Usually, the increase in back-bonding in Ru–CO bonding is connected with a decrease in the IR frequency ν(C≡O). For $[(\eta\text{-}C_5H_4R)Ru(CO)(PPh_3)_2][BPh_4]$ (Table 3), the change in frequency ν(C≡O) in the IR(KBr) spectra is small: 1985 and 1980 cm^{-1} for R = H and R = CH_3, respectively. Introducing five methyl groups into the Cp-ring in the $[(\eta\text{-}C_5Me_5)Ru(CO)(PPh_3)_2]^+$ cation gives a frequency ν(C≡O) of 1959 cm^{-1} and phosphorus atoms resonate at δ 48.8 ppm [10].

The above observations, in all cases, confirm the increase in electron density on ruthenium as a result of introducing a methyl group into the Cp-ring.

The increase in back-bonding in the Ru–CO bond causes an increase in electron density on the oxygen atom in the CO ligand (growth in donor character of the oxygen). On the other hand, the C–O distance increases [9]. A similar argument has been used to explain an upfield shift in the phosphorus atom in PPh_3 in ^{31}P NMR spectra in the case of π-bonding (Scheme 1b). By analogy, in the well-known phenomenon the signal of the benzene ligand in the ^1H NMR spectra of the $[CpRu(\eta^6\text{-}C_6H_6)]^+$ cation is shifted upfield by 1.07 ppm as compared with the proton signal for non-coordinated benzene. A full analogy for upfield shift of the $[CpRu(\eta^6\text{-}C_6H_5F)]^+$ cation in ^{19}F NMR spectra was observed with regard to the signal of fluorine in non-coordinated fluorobenzene [11].

Thus, as a final result of the influence of back-donation of electrons from the ruthenium atom onto the arene ligand in compound X, an increase in the distance

$C_{phenyl\ \pi\text{-bonded}}$–P may be expected. For a similar compound $[CpRu(\eta^6\text{-}C_6H_5)Ph_2PO]ClO_4$, it can be seen that the distance between the phosphorus atom and the carbon atom originating from the π-bonded phenyl ring is longer (1.821 Å) than the other P–C_{phenyl} distances (1.803 and 1.802 Å) [12].

A similar explanation is possible in the case of methyl derivatives in the Cp-ring. Also, the case of formation of the simple $[(\eta^5\text{-}C_5H_4CH_3)Ru(\eta^6\text{-}C_6H_6)]^+$ cation as a result of the rupture of the $C_{phenyl\ \pi\text{-bonded}}$–P bond in compound XI is possible.

In compounds XII–XIV two ruthenium atoms appear, as well as ruthenium σ-bonded to PPh_3 and π-bonded to the phenyl ring of PPh_3. The kind of ruthenium–triphenylphosphine bonding is revealed in the ^{31}P NMR shifts and confirms the above rule. Due to a significant distance from the phosphorus atoms (P^1 and P^2), the R^2-substituent exerts a smaller effect (but distinctly measurable) on the phosphorus signal of PPh_3 than the closer R^1-substituent.

MS(FD) investigations

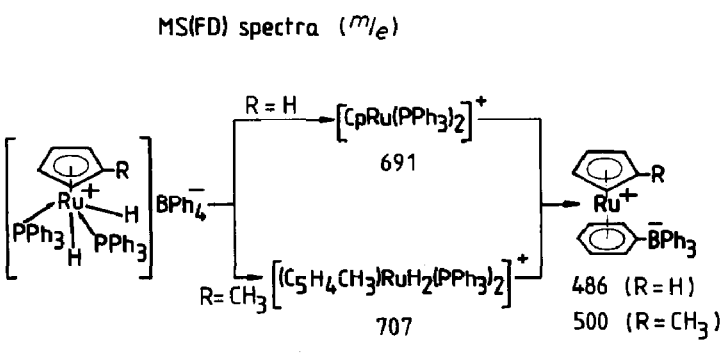
For the example compounds VII–IX (Table 1), the expected signals of the parent ion have been obtained. In the case of ion-pairs V and VI, the following were observed:

(i) a dissociation process, typical for the behaviour of the onium salts; only the cation is detected;

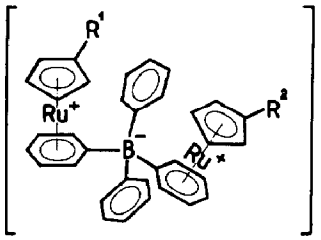
(ii) a reduction–elimination process, connected with loss of 2H, with regard to the signal of the entire cation.

It seems that the R-substituent (Scheme 2) plays an important role in the reaction mechanism. Generally, a methyl substituent located in the Cp-ring favours dissociation (compound VI). The *m/e* 707 signal of the entire cation is observed. For R = H the reduction–elimination process predominates. At prolonged heating times for the MS device emitter, independently of the kind of R-substituent, zwitter-ionic (non-ionic) compounds $(\eta^5\text{-}C_5H_4R)Ru(\eta^6\text{-}C_6H_5)BPh_3$ (*m/e* values 486 or 500, for R = H or R = CH_3, respectively; Scheme 2) were observed.

If the tetraphenylborate anion is present in the ion-pairs then the signal at *m/e* 486 (or 500 for R=CH_3), always connected with the presence of the stable (η^5-cyclopentadienyl)(η^6-tetraphenylborato)ruthenium(II) formed, is observed [7]. Kruger, du Preez and Haines determined, in 1974, the structure of $CpRuBPh_4$ by the X-ray method [13].



Scheme 2



m/e	R^1	R^2
652	H	H
666	H	CH_3
680	CH_3	CH_3

Scheme 3

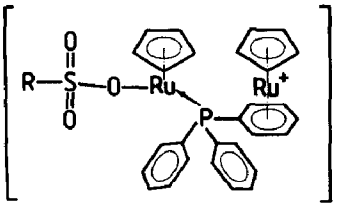
Further MS(FD) investigation of ion-pairs containing the $[BPh_4]^-$ anion was carried out at prolonged heating times and at a higher temperature of the emitter, the next set of signals being obtained around *m/e* 652. For an explanation of this phenomenon, the formation of the dinuclear complex cation with the postulated formula shown in Scheme 3 is proposed. Taking into account the steric situation of the phenyl rings, as shown in the X-ray structure of $CpRuBPh_4$ [13], the formation of the bond of the intermediate $CpRu^+$ cation with one of three phenyl rings, with the creation of new ruthenium π-bonding, is possible. One of the elements of the process giving the dinuclear cation (Scheme 3) must be the dissociation process of the starting compound, giving the intermediate $CpRu^+$ cation with synchronous solvation using the nearest phenyl ring. A similar mechanism of dissociation of $CpRuCl(PPh_3)_2$ in boiling ethylene glycol with the formation of an unstable intermediate $(CpRu)^+$ cation, has already been suggested previously [7]. The compound given in Scheme 3 may be taken as a single-charged cation. By computer simulation of the MS(FD) spectrum for the expected formulae (Scheme 3), support for the suggestion concerning the presence of two ruthenium atoms in the cation investigated has been obtained. The use of methylated derivatives (compound VI) gave sets of signals centred at *m/e* 666 and 680, in agreement with previous assumptions, confirming the proposed formulae in Scheme 3.

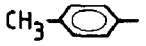
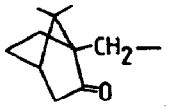
In addition, the use in the MS(FD) investigations of other ion-pairs, for example compound XII, also allows a set of signals to be obtained with a maximum at *m/e* 652.

It may be ascertained that in all of the cases given above, when the set of signals centred at *m/e* 652 was observed, the signals at *m/e* 486 were also present, indicating the presence of $CpRuBPh_4$. It seems that with $CpRuBPh_4$ as the starting compound and at prolonged heating time of the emitter MS device, only the set of signals centred at *m/e* 652 should be obtained. In practice, above *m/e* 486 a sole set of signals centred at *m/e* 652 has been obtained.

Extending the above supposition it seems possible that, in general, every dissociation process giving the unstable $CpRu^+$ cation, which may be solvated by phenyl ring originates, e.g. from compounds VII or VIII, finally gives the new stable complex cation. The experiments carried out using compounds VII and VIII gave the expected new group signals (besides the signals of the parent ion) with maxima at *m/e* 767 and 827 for compounds VII and VIII, respectively, confirming this suggestion. Scheme 4 shows the postulated structure of the dinuclear complex cation, which forms as a result of the following steps: (i) dissociation of one PPh_3 molecule from compounds VII or VIII;

(ii) a further dissociation process giving the intermediate $CpRu^+$ cation;



m/e	R
767	
827	

Scheme 4

(iii) synchronous solvation of the intermediate $CpRu^+$ cation by formation of a π-bond with the nearest phenyl ring originating from starting compounds VII or VIII.

Step (i) is not necessary, because in the MS(FD) spectra the set of signals centred at *m/e* 1089 has also been found. It is probable that the addition of the $CpRu^+$ cation to the entire starting molecule is also possible. The use of methylated derivatives (compound IX) in several cases gave sets of signals centred at *m/e* 1103 and 1117 (and *m/e* 841 and 855 for $-PPh_3$). This observation also confirms the presence of two Cp-rings in the postulated structure of the complex cation (Scheme 4). At present, it appears that partial confirmation of the mechanism of formation of compounds XII–XIV in boiling ethylene glycol medium [7] is achieved.

Conclusions

Actually, the $[CpRuH_2(PPh_3)_2][sulphonate]$-type ion-pairs obtained with yields of nearly 100% give, in the reduction–elimination process, new covalent compounds of type $CpRu(sulphonate)(PPh_3)_2$, in which the bond of the sulphonate group from oxygen to the ruthenium atom is postulated. The new compounds obtained are stable in the solid, crystalline state, being resistant to the action of air and water and having melting points of about 200 °C. Proceeding according to the above method, it is possible to join optional organic substituents (aromatic or aliphatic) to the $CpRu(PPh_3)_2$ group via the sulphonate group.

When the organic substituent is chiral (compounds VIII and IX), the ruthenium atom will be prochiral. In solutions of these compounds, the inequivalence of phosphorus atoms P^1 and P^2 should be observed. For example, the ^{31}P NMR spectrum in benzene consists of doublets of doublets. Moreover, in the circular dichroism (CD) spectrum (in benzene), bands at λ_{max} 343 and 400 nm in the negative parts of the spectrum and a band at 483 nm in the positive parts of the spectrum are shown. When using $CHCl_3$ or MeOH as solvents, the diastereotopic inequivalence of the phosphorus atoms is not observed.

Experimental

General experimental conditions and apparatus are similar to those described in previous parts of this series (see ref. 5). Also, the Bruker ^{31}P NMR (121.49 MHz) apparatus was used. Almost all of the off-resonance ^{1}H-decoupled ^{31}P NMR spectra cited in the present paper were obtained using Bruker apparatus.

i. Preparation of [CpRuH$_2$(PPh$_3$)$_2$][SO$_3$C$_6$H$_4$Me] (I). 0.3950 g of CpRuH(PPh$_3$)$_2$ (0.57 mmol), 0.1842 g of *p*-toluenesulphonic acid $C_7H_6O_3S \cdot H_2O$ (0.97 mmol) and 10 cm^3 of MeOH were stirred at room temperature for 5 min. The resultant clear, yellow solution contained practically only the $[CpRuH_2(PPh_3)_2]^+$ cation and *p*-toluenesulphonate anion. After about 0.5 h of storage the concentration of the $[CpRuH_2(PPh_3)_2]^+$ cation fell to 70 mol%, and after 1 day of storage to 55% of the initial value.

ii. Preparation of [CpRuH$_2$(PPh$_3$)$_2$][SO$_3$C$_{10}$H$_{15}$O] (II). 0.7325 g of CpRuH(PPh$_3$)$_2$ (1.06 mmol), 0.3094 g of *d*(+)campho-10-sulphonic acid $C_{10}H_{16}O_4S \cdot H_2O$ (1.23 mmol) and 30 cm^3 of MeOH were stirred at room temperature for 10 min. Also, as in (i), the diminution of the concentration of complex cation against time is 74 and 54% after storage for 0.5 h and 1 day, respectively.

iii. Preparation of [(η-C$_5$H$_4$Me)RuH$_2$(PPh$_3$)$_2$][SO$_3$C$_6$H$_4$Me] (III). The procedure was similar to that for I, using (η-C$_5$H$_4$Me)RuH(PPh$_3$)$_2$ instead of CpRuH(PPh$_3$)$_2$.

iv. Preparation of [(η-C$_5$H$_4$Me)RuH$_2$(PPh$_3$)$_2$][SO$_3$C$_{10}$H$_{15}$O] (IV). 0.3595 g of (η-C$_5$H$_4$Me)RuH(PPh$_3$)$_2$ (0.51 mmol), 0.1525 g of *d*(+)campho-10-sulphonic acid (0.61 mmol) and 15 cm^3 of MeOH were stirred at room temperature for 5 min. The resultant yellow solution contained compound IV.

v. Preparation of [CpRuH$_2$(PPh$_3$)$_2$][BPh$_4$] (V). To a solution containing [CpRuH$_2$(PPh$_3$)$_2$][SO$_3$C$_{10}$H$_{15}$O] (compound II), prepared as in (ii), a solution of 0.50 g of NaBPh$_4$ in 10 cm^3 of MeOH was added. The resultant white–yellow precipitate was shaken for 5 min, filtered, then washed with 15 cm^3 of MeOH and 10 cm^3 of n-hexane. After drying, 0.9548 g of V was obtained. IR(KBr): 3062m, 2991w, 2074vw 2048vw ν(Ru–H); 1588m, 1490s, 1444vs, 1320w, 1278w, 1192w, 1100s, 1041m, 1010m, 925w, 846s, 753m, 742s, 708vs, 616s, 544s, 528vs, 516m, 500m, 468m, 443m cm^{-1}.

vi. Preparation of [(η-C$_5$H$_4$Me)RuH$_2$(PPh$_3$)$_2$][BPh$_4$] (VI). To a solution containing [(η-C$_5$H$_4$Me)RuH$_2$(PPh$_3$)$_2$][SO$_3$C$_{10}$H$_{15}$O] (compound IV) prepared as in (iv), a solution of 0.25 g of NaBPh$_4$ in 5 cm^3 of MeOH was added. The procedure is then the same as for (v). 0.4625 g of VI was obtained. IR(KBr): 2068vw, 2042vw cm^{-1} ν(Ru–H). The IR spectrum is practically identical with the spectrum of compound V.

vii. Preparation of CpRuOSO$_2$C$_6$H$_4$Me(PPh$_3$)$_2$ (VII). 0.3950 g of CpRuH(PPh$_3$)$_2$ (0.57 mmol), 0.1842 g of *p*-toluenesulphonic acid (0.97 mmol) and 10 cm^3 of MeOH were stirred at room temperature for 5 min. Next, the resulting clear, yellow solution was evaporated to dryness at 45 °C under reduced pressure, the residue was dissolved in 10 cm^3 of benzene and then chromatographed (silicagel, benzene). The first yellow fraction (ca. 100 cm^3 of volume) was collected and evaporated to dryness yielding a vitreous, lemon yellow substance (0.3455 g). This substance was treated with 50 cm^3 of n-hexane and left standing overnight. Next, the substance was pulverized, filtered and washed with n-hexane and, after drying,

0.1245 g of VII was obtained. IR(KBr): 3060m, 1480s, 1435s, 1258vs, 1188m, 1158s, 1112s, 1093w, 1030m, 1000vs, 842m, 820m, 750s, 697vs, 680w, 576w, 567w, 532m, 516s, 502w, 462m, 418m cm^{-1}.

viii. Preparation of $CpRuOSO_2C_{10}H_{15}O(PPh_3)_2$ *(VIII).* 1.0941 g of CpRuH$(PPh_3)_2$ (1.58 mmol), 0.4462 g of *d*(+)campho-10-sulphonic acid (1.78 mmol) and 40 cm^3 of MeOH were stirred at room temperature for 30 min. The solution was evaporated to dryness at 45 °C under reduced pressure, obtaining 1.6081 g of yellow substance. 30 cm^3 of benzene were added and, after dissolution, 100 cm^3 of n-hexane. The mixture was immediately filtered and to the filtrate yet another 10 cm^3 of n-hexane were added. After 1 day of storage the compound was pulverized and filtered, yielding 0.4647 g of VIII. IR(KBr): 3063bm, 2949bm, 1756vs cm^{-1} ν(C=O); 1490s, 1446s, 1278bm, 1208bm, 1158s, 1099s, 1060m, 1018vs, 848m, 818m, 760m, 750m, 707vs, 613m, 592m, 538w, 525vs, 515s, 502m, 467m, 422bm cm^{-1}.

ix. Preparation of $(\eta\text{-}C_5H_4Me)RuOSO_2C_{10}H_{15}O(PPh_3)_2$ *(IX).* The procedure is similar to procedure viii, using the methyl derivative of CpRuH$(PPh_3)_2$ as substrate.

x. The $[CpRuH_2(PPh_3)_2]$*[sulphonate]–*HX_{aq}*–MeOH system.* 0.1076 g of CpRuH$(PPh_3)_2$ (0.15 mmol), 0.0603 g of *d*(+)campho-10-sulphonic acid (0.24 mmol) and 10 cm^3 of MeOH were stirred for 20 min at room temperature. Next, 0.2 cm^3 of 12 *M* HCl_{aq} (2.4 mmol) was added and left in storage for 4 days. The resultant orange crystals were separated, 0.0453 g of CpRuCl$(PPh_3)_2$, m.p. 206–248 °C, 40% yield, were obtained. For HBr_{aq} the procedure was similar, obtaining CpRuBr$(PPh_3)_2$, m.p. 228–255 °C, 90% yield.

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