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CYCLOPENTADIENYL-RUTHENIUM COMPLEXES

I. THE REACTIVITY OF SOME π-CYCLOPENTADIENYL-BISTRIPHENYLPHOSPHINE-RUTHENIUM(II) COMPLEXES

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Summary

Several ruthenium complexes of the $CpRuX(PPh_3)_2$ type, where X = Cl, Br, I, NCS, NCO, CN, BH_4, H, D, and some of the $CpRuS_2CZ(PPh_3)$ type, where Z = NR_2 or OR, were obtained. The hydride $CpRuH(PPh_3)_2$ was obtained in high yield by reaction of $CpRuCl(PPh_3)_2$ with ROM (R = alkyl, M = alkali metal). The other complexes were obtained by ligand exchange of the chloride or hydride with MX salts or HX acids, respectively. Reaction of chloride or hydride with cyclopentadiene led to ruthenocene. However, when pyrrole was used instead of cyclopentadiene, it was not possible to obtain azaruthenocene in this way.

Introduction

Wilkinson in 1969, and later Bruce et al. [1—3] synthesized an interesting group of compounds I—V (see page 90). Our attempts to repeat Bruce's synthesis [2—3] of the orange compound I, melting at 131—135°C were unsuccessful. We obtained an orange product I melting at 236—248°C in a sealed capillary, which in an open capillary began melting at 135—138°C and was completely melted at 180—200°C. The orange compound formed independently of whether the reaction was conducted in absolute or 95% ethanol, in the presence or absence of oxygen (under argon), of the kind of ruthenium(III) chloride used in the synthesis, or the kind of solvent used for crystallization.

Our complex I gave the derivatives II—XV whose properties are listed in Tables 1 and 2. It is of interest that the derivatives II—V obtained by us from compounds I or V melt at higher temperatures than do the compounds ob-

(*Continued on p. 90*)

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TABLE 1

YIELDS, MELTING POINTS AND MASS SPECTRAL DATA FOR COMPOUNDS ISOLATED

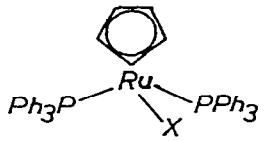
Compound		Mol. wt. (calcd.)	MS(FD) Parent ion m/e [a]	Colour	Yield (%)	M.P. (°C)	Substrate used for syntheses with I or V
I	$CpRuCl(PPh_3)_2$	726.2	726	orange	90	236—248	
II	$CpRuBr(PPh_3)_2$	770.6	771	orange	97	212—218	HBr
III	$CpRuI(PPh_3)_2$	817.6	818	deep red	97	228—234	HI
IV	$CpRuBH_4(PPh_3)_2$	705.6	706	ash grey	30	145—150	$NaBH_4$
V	$CpRuH(PPh_3)_2$	691.7	692	yellow	88	181—184	MeONa
VII	$CpRuNCS(PPh_3)_2$	748.8	749	golden	89	202—204	KSCN
VIII	$CpRuNCO(PPh_3)_2$	732.7	733	dark yellow	83	254—257	KOCN
IX	$CpRuCN(PPh_3)_2$	716.7	717	yellow	91	268—271	KCN
X	$CpRuS_2C—OMe(PPh_3)_2$	797.9	798 [b]	yellow orange	89	119—120	$MeO—CS_2K$
XI	$CpRuS_2C—OEt(PPh_3)$	549.6	550 [b]	yellow orange	72	150—153	$EtO—CS_2K$
XII	$CpRuS_2C—O—n\text{-}Pr(PPh_3)$	563.6	564 [b]	yellow orange	99	105—107	$n\text{-}PrO—CS_2K$
XIII	$CpRuS_2C—O—n\text{-}Bu(PPh_3)$	577.6	578 [b]	yellow orange	48	75— 78	$n\text{-}BuO—CS_2K$
XIV	$CpRuS_2C—NEt_2(PPh_3)$	576.7	577 [b]	yellow orange	91	173—177	$Et_2N—CS_2Na \cdot 3\,H_2O$
XV	$CpRuS_2C—N(CH_2)_4(PPh_3)$	574.7	575 [b]	yellow orange	95	218—222	$(CH_2)_4N—CS_2NH_4$

[a] Data for ^{102}Ru isotope; [b] MS(EI).

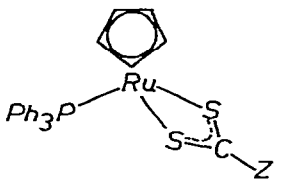
TABLE 2

NMR DATA OF CYCLOPENTADIENYL RUTHENIUM COMPLEXES. CHEMICAL SHIFTS (δ, ppm)

Compound		Solvent	^{1}H NMR (TMS)			^{31}P NMR (H_3PO_4)
			P—C_6H_5	C_5H_5	Others	
I	$CpRuCl(PPh_3)_2$	CS_2	7.06m	3.89s		
		C_6D_6	7.61m, 6.86m	4.06s		
		CH_2Cl_2				38.6s
II	$CpRuBr(PPh_3)_2$	CS_2	7.11m	3.92s		
		C_6D_6	7.34m, 6.66m	3.89s		
III	$CpRuI(PPh_3)_2$	CS_2	7.07m	3.99s		
		C_6D_6	7.22m, 6.66m	3.89s		
		CH_2Cl_2				36.2s
IV	$CpRuBH_4(PPh_3)_2$	CS_2	7.21m, 7.36m	4.79s		
V	$CpRuH(PPh_3)_2$	CS_2	6.97m	4.06s		
		C_6D_6	7.33m, 6.76m	4.26s		
		$CDCl_3$	7.18m	4.09s		
		CH_2Cl_2			Ru—H: −11.5t, $J(^1H—^{31}P)$ 34.0Hz	67.1s
VII	$CpRuNCS(PPh_3)_2$	CS_2	7.16m	4.06s		
		C_6D_6	7.29m, 6.86m	3.89s		
VIII	$CpRuNCO(PPh_3)_2$	CS_2	7.12m	3.92s		
IX	$CpRuCN(PPh_3)_2$	CS_2	7.11m	4.16s		
X	$CpRuS_2C—OMe(PPh_3)_2$	CS_2	7.00m	4.20s	OCH_3: 3.75s	
XI	$CpRuS_2C—OEt(PPh_3)$	CS_2	7.47m	4.37s	OCH_2: 4.00q; CH_3: 1.13t	
XII	$CpRuS_2C—O—n\text{-}Pr(PPh_3)$	CS_2	7.13m	4.22s	OCH_2: 3.70t; CH_2: 1.50m; CH_3: 0.94m	
XIII	$CpRuS_2C—O—n\text{-}Bu(PPh_3)$	CS_2	7.50m	4.40s	OCH_2: 3.95t; C_3H_7: 1.00m	
XIV	$CpRuS_2C—NEt_2(PPh_3)$	CS_2	7.43m	4.23s	NCH_2: 3.35q; CH_3: 0.88t	
XV	$CpRuS_2C—N(CH_2)_4(PPh_3)$	CS_2	7.23m	4.12s	NCH_2: 3.07m; CH_2: 1.70m	



	X		X
I	Cl	VI	D
II	Br	VII	NCS
III	I	VIII	NCO
VI	BH_4	XI	CN
V	H	X	S_2C-OMe



	Z
XI	O-Et
XII	O-n-Pr
XIII	O-n-Bu
XIV	NEt_2
XV	$N(CH_2)_4$

tained previously [1,2]. The melting temperature did not change after crystallization of the compounds.

If the structure of the complexes obtained is assumed to be similar to the structure of the isoelectronic rhodium cation $[(C_5Me_5)RhH(PPh_3)_2]^+$ [14] the possibility of our compound I and that described in the literature [1—3] being isomers can be excluded.

Results and discussion

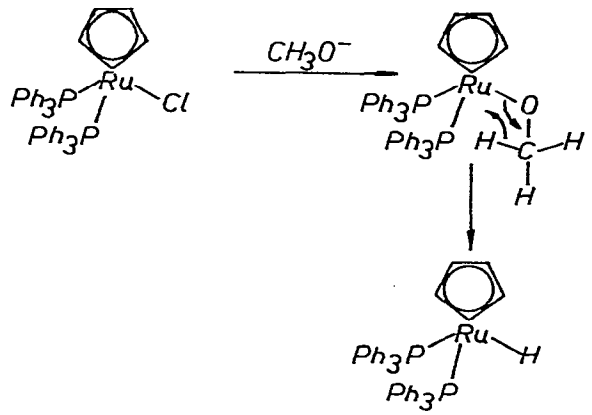
Our studies on the reaction between our compound I and bases shown that product I reacts particularly readily with alcoholates to give the hydride V whose melting temperature differs from that of compound obtained by Bruce, whereas the IR and NMR spectra of the two compounds are identical [2].

Hydride V is obtained the most easily and in very high yield from the reaction of I with sodium or potassium methoxide in methanol. It can also be obtained, though less pure and in lower yield, in ethanol in the presence of sodium ethoxide, whereas it cannot be obtained in t-butanol in the presence of sodium t-butoxide. It can be concluded therefore that the reaction consists of a nucleophilic action of the alkoxylate anion on compound I, resulting in formation of the alkoxy complex in which there occurs an intramolecular hydride shift giving hydride V as final product (Scheme 1).

That mechanism was confirmed by a reaction performed in CH_3OD and CD_3OD in the presence of sodium methoxide or deuteromethoxide, respectively. The former reaction afforded only hydride V, the later only deuteride VI. The mechanism of that reaction is therefore analogous to that described by Vaška for iridium complexes [4].

The supposition of a nucleophilic action of the alkoxylate ion should find confirmation in reaction of I with other nucleophilic reagents.

Actually, compound I reacted very readily with type MX salts (where M =



SCHEME 1

Na, K; X = I, NCS, NCO, CN, BH_4) in methanol by replacing the chloride ligand with X (III, VII—IX).

The structure of complexes VII—IX has been confirmed by mass spectra, and ^1H NMR and IR spectra. The IR spectra of VII—IX show a very strong C—N stretching frequency band at 2100, 2225 and 2070 cm^{-1}, respectively, which permits assignment to the complexes of the structures suggested. The IR spectra of similar complexes had been discussed by a number of investigators [5,6,8—10].

Xanthates X—XIII and dithiocarbamate complexes XIV—XV were obtained analogously from compound I. In the reaction of I with sodium methylxanthate complex X was obtained, in which the chlorine atom is substituted by the S_2COMe group, and two phosphine ligands remain unsubstituted. In contrast, the reaction of ethyl-, n-propyl- and n-butylxanthates and dithiocarbamates with I occurs simultaneously with substitution of the chlorine atom and of one phosphine group by the S_2CCR or S_2CNR_2 group giving rise to the chelate complexes XI—XV. This is seen clearly from the integration of the phenyl group protons in the ^1H NMR spectra and from mass spectra.

The band at 1040 cm^{-1}, which is characteristic of the C—S stretching frequency [12,13] appears in the IR spectra of complexes X—XIII and of the starting xanthates. The dithiocarbamates show an analogous band at 1000 cm^{-1}.

We also examined the possibility of converting compound I into ruthenocene. Heating of a benzene solution of compound I for 4 hours at boiling temperature leads to ruthenocene in 0.4% yield. Yields are increased to 34% by addition of cyclopentadiene and to about 50% by addition of equimolar amounts of cyclopentadiene and sodium hydride (Fig. 1). The mechanism of that reaction is unclear. It may be that ruthenocene forms owing to the action of the cyclopentadienide ion on complex I, or to the action of cyclopentadiene on hydride V, which eventually forms during the reaction. However under no circumstances have we been able to obtain ruthenocene in higher yields. When pyrrole was used instead of cyclopentadiene it was impossible to obtain azaruthenocene in this way.

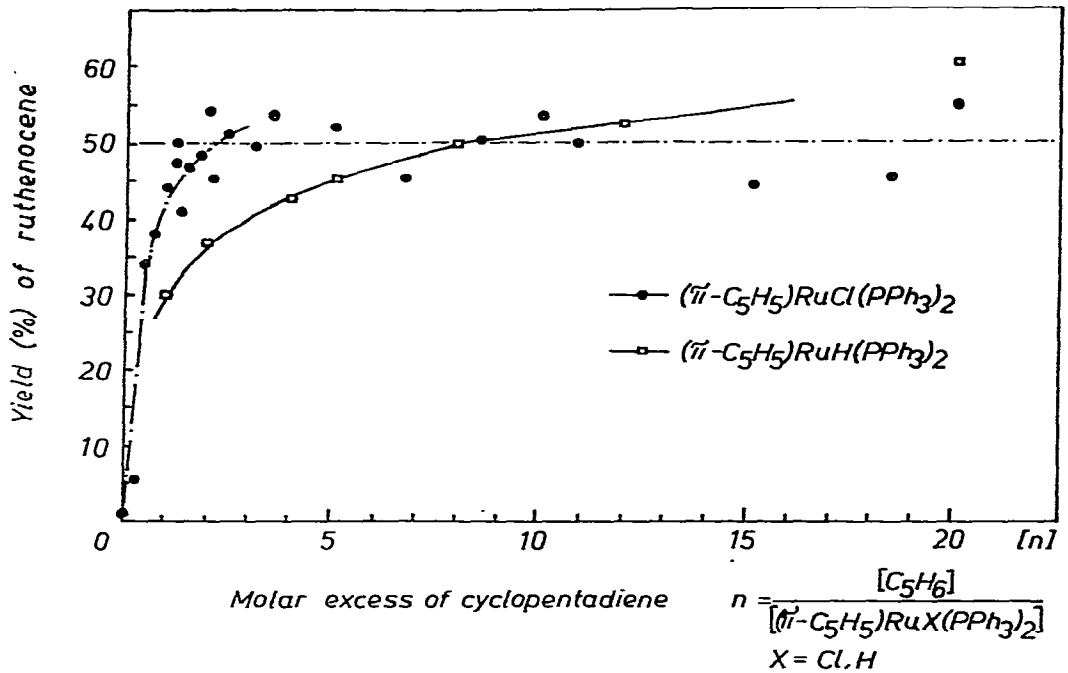


Fig. 1. Dependence of the yield of ruthenocene on molar excess of cyclopendatiene in the reaction of chloride I or hydride V.

Hydride V is, beside the chloride, a convenient substrate for obtaining complexes in which the hydride ligand is replaced by another ligand.

The simplest reaction of hydride V is performed with protic acids, resulting in ligand exchange and simultaneous liberation of hydrogen [c.f. 7]. Thus, compounds I—III and VII were obtained by reaction of V with HCl, HBr, HI and HSCN in methanol. Attempts to obtain a fluoride complex in the same manner failed. All compounds obtained had higher melting temperatures than their literature analogues [1,2].

Reaction of hydride V with cyclopentadiene and excess sodium hydride leads to ruthenocene, similarly as in the case of chloride I (Fig. 1).

Hydride V reacts with trichloroethanol but not with trifluoroethanol to regenerate chloride I. Compound I was obtained either as a high-melting or a low-melting product, depending on the procedure employed. The two forms had identical ^{1}H NMR spectra and R_F values.

The reaction presumably takes the following course:

(i) formation of the alkoxy complex and elimination of hydrogen,

(ii) regeneration of hydride V and formation of chloral,

(iii) reduction of chloral with the hydride ion and elimination of hydrogen chloride,

(iv) formation of I from hydride V and hydrogen chloride.

This mechanism is confirmed by the fact that a reaction of hydride V with chloral also leads to compound I.

The ^{1}H NMR spectra of the complexes obtained showed two signals, namely

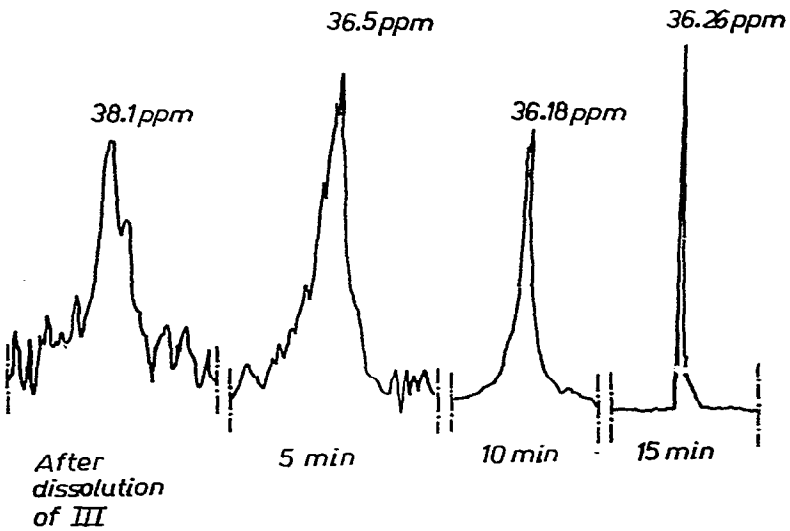


Fig. 2. Changes in the ^{31}P NMR spectrum of $CpRuI(PPh_3)_2$ with time.

a sharp singlet at about 4 ppm (δ) from 5 protons of the cyclopentadienyl ring, and a multiplet at about 7 ppm from 30 protons of the phenyl groups. Slight shifts of these signals occuring with change of ligand X are summarized in Table 2.

The ^{31}P NMR spectra of complexes I, III and V in methylene chloride showed one sharp signal indicating that the two triphenylphosphine ligands were equivalent. These signals did not change within the —80 to 35° C temperature range. However, the spectrum observed for compound III immediately after dissolution was a broad signal with 38.1 ppm shift and changed after few minutes into an equally broad signal at 36.5 ppm, which retained a residual signal at 38.1 ppm (Fig. 2). After a further 10 minutes there appeared a sharp singlet with the established chemical shift at 36.2 ppm, which did not change with decrease of temperature. This can be accounted for by either a slow solvation equilibrium or a slow change in ligand orientation in the complex.

The molecular formulae of compounds I—X were confirmed by mass spectrometry using the FD technique. In the electron impact mass spectra the parent ions of compounds XI—XV are easily detectable and the main fragmentation path may be summarized as follows:

$$[CpRuS_2CZ(PPh_3)]^+ \xrightarrow{-PPh_3} [CpRuS_2CZ]^+ \xrightarrow{-CZ} \underset{231}{[CpRuS_2]^+} \rightarrow \underset{167}{[CpRu]^+} \rightarrow \underset{102}{[Ru]^+}$$

Experimental

IR spectra were recorded on a Perkin-Elmer model 577 spectrophotometer using Nujol mulls and KBr pellets. ^1H NMR spectra were recorded at 60 MHz using Tesla BS 467 and Perkin-Elmer R 12 B spectrometers. ^{31}P NMR spectra were recorded on a JEOL JNM-FX 60 apparatus. Mass spectra were recorded

on a Varian MAT 711 mass spectrometer using the FD technique at 8 + 3 kV, and on a JEOL JMS-D100 at ionizing voltage equal 75 eV.

Melting points were measured in sealed capillaries and were uncorrected.

Preparation of $CpRuCl(PPh_3)_2$ (I)

$CpRuCl(PPh_3)_2$ (I) was prepared according to known methods [3].

To a boiling solution of triphenylphosphine (16.8 g, 64 mmol) in 95% ethanol (800 cm^3) was added a 0.2 *M* solution of $RuCl_3 \cdot aq$ in 95% ethanol (80 cm^3, 16 mmol). After 5 min refluxing freshly distilled cyclopentadiene (20 cm^3) and 95% ethanol (130 cm^3) were added. The solution was refluxed for 1 hour and cooled to give orange crystals which were collected and washed with ethanol. Yield 10.5 g, m.p. 236—248°C. Recrystallization from dichloromethane/n-hexane mixture gave compound I, melting at 234—242°C. Found: C, 67.4; H, 4.7; Cl, 4.8; $C_{41}H_{35}P_2ClRu$ calcd.: C, 67.8; H, 4.86; Cl, 4.88%. IR: ν(Ru—Cl) 280m, 275m cm^{-1}.

Preparation of $CpRuH(PPh_3)_2$ (V)

A mixture of 2 g of I and 100 cm^3 of a 0.2 *M* solution of CH_3ONa in anhydrous methanol was stirred vigorously at room temp. for 1.5 h, then was heated to 50°C and stirred for another 0.5 h. After cooling in an ice/water bath, the yellow precipitate was collected, washed with methanol and hexane, and dried over KOH; yield 1.68 g. Found: C, 71.2; H, 5.3; Cl, 0.00; $C_{41}H_{36}P_2Ru$ calcd.: C, 71.2, H, 5.25; Cl, 0.00%. IR: ν(Ru—H) 1968m cm^{-1}.

Preparation of $CpRuD(PPh_3)_2$ (VI) was like that of V, using sodium deuteromethoxide in CD_3OD. IR: ν(Ru—D) 1405m cm^{-1}.

Preparation of $CpRuBr(PPh_3)_2$ (II)

To a suspension of V (0.692 g, 1 mmol) in 20 cm^3 of methanol was added an excess of hydrogen bromide (0.5 cm^3, 40% solution). The mixture was refluxed for 5 min. After complete dissolution of V orange crystals of II had precipitated. The product was collected and washed with methanol. Yield 0.75 g.

Preparation of $CpRuI(PPh_3)_2$ (III)

Complex III was prepared analogously using hydrogen iodide (0.6 cm^3 of 40% aqueous solution of HI). Yield 0.795 g.

Preparation of $CpRuBH_4(PPh_3)_2$ (IV)

To a suspension of I (0.50 g, 0.68 mmol) in 20 cm^3 of tetrahydrofuran was added an excess of well powdered $NaBH_4$ (0.10 g). The mixture was refluxed for 1.5 h, then cooled and filtered. After evaporation of the filtrate the mixture was extracted with benzene. Crystallization from diethyl ether gave ash-grey crystals of IV. Yield 0.15 g.

Preparation of $CpRuNCS(PPh_3)_2$ (VII)

To a suspension of I (0.363 g, 0.5 mmol) in 10 cm^3 of methanol was added an excess (100 mg, 1 mmol) of potassium thiocyanate. The mixture was refluxed for 1 h. The yellow crystals of VII precipitated during that time were collected, washed with methanol and hexane, and dried over KOH. Yield

0.332 g; m.p. 202—204°C. IR: 3052m, 2100vs, 1585w, 1569w, 1478s, 1430s, 1310w, 1265w, 1180m, 1151m, 1089s, 1069w, 1024m, 996m, 850w, 837m, 803m, 755m, 740s, 696vs, 618w, 591w, 536s, 524vs, 514vs, 499s, 468m, 423m, 361w, 336vw, 268vw cm^{-1}.

Preparation of $CpRuNCO(PPh_3)_2$ (VIII)

A suspension of I (0.415 g, 0.57 mmol) and 0.072 g (0.89 mmol) of KOCN in 6 cm^3 of methanol was refluxed for 1.5 h. After cooling the dark yellow precipitate was filtered off, washed with methanol and dried. Yield 0.349 g; m.p. 254—257°C. IR: 3055m, 2225vs, 1583w, 1570w, 1479s, 1430s, 1416w, 1308s, 1179m, 1153m, 1102w, 1088s, 1082s, 1068m, 1028m, 1005m, 995m, 860w, 849w, 833m, 807m, 753s, 740s, 692vs, 680m, 618w, 589m, 533s, 520vs, 502s, 465m, 436w, 423m, 373w, 335w, 320w, 275vw cm^{-1}.

Preparation of $CpRuCN(PPh_3)_2$ (IX)

A suspension of I (0.409 g, 0.56 mmol) and potassium cyanide (0.145 g, 2.3 mmol) is 6 cm^3 of methanol was refluxed for 2 h. After cooling, the yellow precipitate was collected, washed with methanol and dried. Yield 0.367 g (91%); m.p. 268—271°C. IR: 3055m, 2078s, 2065s, 1583w, 1570w, 1479s, 1432vs, 1310w, 1268w, 1184m, 1153m, 1085s, 1068w, 1053w, 1026w, 997m, 850w, 830m, 810m, 760m, 753m, 740m, 694vs, 618w, 598w, 540s, 525vs, 518vs, 500s, 474m, 460w, 435m, 419m, 350w cm^{-1}.

Reaction of hydride V with trichloroethanol

a) 0.296 g (0.43 mmol) of hydride V in 3.5 cm^3 of methanol was heated under reflux with 0.14 g (0.9 mmol) of trichloroethanol for 1 h. After that time a further 8.3 mmol of trichloroethanol was added and the mixture was refluxed for another 1 h. The crystals were collected and washed 3 times with 2 cm^3 of methanol. Yield of the orange-coloured chloride I 92%; m.p. 242—248°C.

b) To 0.355 g (0.51 mmol) of hydride V in 3 cm^3 of methanol was added 1.5 cm^3 (15.6 mmol) of trichloroethanol and the mixture was heated under reflux until turned dark, and cooled. After a few minutes the yellow microcrystals of chloride I had precipitated. The crystals were collected, washed with methanol and dried. Yield of I 0.125 g (33%); m.p. 131—138°C.

The ^1H NMR and IR spectra of the two compounds (the yellow and the orange) were identical. The yellow compound was obtained in only a few cases.

Reaction of hydride V with chloral

A mixture of Cl_3CCHO (0.092 g, 0.62 mmol), 3 cm^3 of methanol and 0.168 g (0.24 mmol) of hydride V was stirred with heating at 60—65°C for 25 min. After the solution was cooled the orange crystals of chloride I precipitated. Yield 0.09 g (51%); m.p. 240—242°C.

Preparation of ruthenocene

a) To a suspension of 1 mmol of I or V in 50 cm^3 of benzene were added various amounts (see Fig. 1) of freshly distilled cyclopentadiene and about 0.2 g of NaH. The mixture was stirred and left for 5 days at room temperature. The solid was collected and the filtrate was chromatographed on 10 g of silica

gel. The column was washed with benzene and 100 cm^3 of colourless benzene solution was obtained. The solvent was removed under reduced pressure to obtain ruthenocene as a colourless solid. Yield about 50%.

b) To a suspension of 1 mmol of I or V in 50 cm^3 of benzene was added 2 mmol of freshly distilled cyclopentadiene and about 0.2 g of NaH. The mixture was refluxed for 4 h. After that time the ruthenocene was isolated in the same way as in procedure a). Upon evaporation of the first 100 cm^3 of benzene eluate was obtained 0.12 g of colourless ruthenocene. Yield 50—55%; m.p. 198—201°C.

It is possible to use toluene or n-hexane instead of benzene. Metallic sodium or potassium can be used instead of sodium hydride. Pure ruthenocene was always obtained by chromatography.

Preparation of $CpRuS_2CZ(PPh_3)$ (X—XV)

To a suspension of I (0.60 g, 0.82 mmol) in 10 cm^3 of methanol was added an excess (0.9—1.1 mmol) of dithiocarbamate (in XIV and XV) or xanthate (in X—XIII) of alkali metal or ammonium. The mixture was refluxed for 15—25 min. Only XII was heated for 3 h at 50°C. After cooling, the precipitate was filtered off, washed with methanol then with n-hexane and dried over KOH. Yield 48—99% (see Table 1).

Acknowledgments

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