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Pentamethylcyclopentadienylruthenium complexes

IV *. Pentamethylcyclopentadienyl(halo)ruthenium(III, III/II, or II), and pentamethylcyclopentadienyl(alkoxo)ruthenium(II) complexes

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Abstract

Treatment of $[Cp^\star RuCl_2]_2$ (**1a**) ($Cp^\star = \eta^5$-C_5Me_5) with NaBr or KI leads to the complexes $[Cp^\star RuBr_2]_2$ (**1b**) and $[Cp^\star RuI_2]_2$ (**1c**). Reduction of these Ru^{III} halides with cobaltocene gives pentane-soluble, paramagnetic, molecular mixed valence $Ru^{III/II}$ complexes $[Cp^\star Ru(\mu$-$X)_3RuCp^\star]$ (**3a**, **3b**, **3c**) and on further reduction $Cp^\star Ru^{II}$ halides $[Cp^\star RuX]_n$ (**4a**, **4b**, **4c**; X = Cl, Br, I).

Treatment of **1a** with alcohol in the presence of K_2CO_3 gives the Ru^{II} alkoxo complexes $[Cp^\star RuOR]_2$ (**16a–16d**; $R = CH_3$, C_2H_5, C_3H_7, C_4H_9). **16a** gives **4a** upon treatment with Me_3SiCl. The spectroscopic characteristics, physical properties and cleavage and complexation reactions of the halo and alkoxo complexes are described.

Introduction

The preparation of $[Cp^\star RuCl_2]_n$, (**1a**, $Cp^\star = \eta^5$-C_5Me_5) from $RuCl_3 \cdot H_2O$ in methanol (by Tilley, Grubbs and Bercaw [2] and by Suzuki and coworkers [3]) (by a procedure analogous that used for the synthesis of $[Cp^\star RhCl_2]_2$ by Booth and Hazeldine [4]) opened a new route into $Cp^\star Ru$ chemistry which has presently been exploited by several groups. Interesting species obtained from **1a** include the $Cp^\star$ analogue [5,6] of the trihydride complex $CpRuPPh_3H_3$ [7], the transition metal silylene complex $Cp^\star Ru(PMe_3)_2(SiPh_2)(NCCH_3)$ [8], and a coordinatively unsaturated complex with a bulky phosphine, $Cp^\star RuP(C_6H_{11})_3Cl$ [9].

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* For part III see ref. 1.

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Complex **1a** is frequently formulated as a polymer or oligomer with the number of units, *n*, unspecified, and though it is available in several laboratories little information on its properties has been presented. A notable feature in the the original work was the ease of reduction of **1a** on treatment with phosphines to give the complexes $Cp^{\star}RuL_2X$ [2]. This type of reduction seems to occur frequently when **1a** is treated with acceptor ligands L (phosphines or olefins) in alcohols [3]. Similarly, reaction of **1a** with allyl halides in ethanol affords $Cp^{\star}Ru(\pi\text{-allyl})Cl_2$ [10]. The Ru^{III} oxidation state was preserved only on cleavage of **1a** with PPh_3 [6] or when the Cl ligands in **1a** were substituted for RS groups [11].

Polymeric Ru^{IV} complexes $Cp^{\star}RuX_3$ (X = Cl, Br, I) were made by action of halogens on **1a** and they have been converted into either $Cp^{\star}Ru^{IV}X_3L$ or $Cp^{\star}Ru^{III}X_2L$ derivatives depending on the halogen X and the ligand L [12]. In spite of these indications that there is an extensive pentamethylcyclopentadienyl chemistry of ruthenium awaiting development, many of the more fundamental materials have not been subjected to detailed spectroscopic and physical characterization. Moreover, the ligand/halide combination most appropriate for stabilization of a particular oxidation state has not been defined clearly, and the absence of knowledge of dependence of the redox chemistry on the coligands makes it difficult to rationalize or predict the course of reactions.

In the course of our studies on $Cp^{\star}M$-halogeno complexes [13–15] we decided to investigate the chemistry of species containing the $Cp^{\star}RuX_n$ moiety using **1a** as a starting point. In line with our previous strategy, we aimed to generate "ligand-free" lower oxidation state $Cp^{\star}Ru$-halides, $(Cp^{\star}RuX_m)_n$, which might be transformed into a wide variety of organometallic complexes by simple addition of appropriate ligands. A preliminary account of some aspects of the work has appeared [1].

Results

Ru^{III} halides $[Cp^{\star}RuX_2]_2$ (X = Cl, Br, I; 1a–c)

Complex **1a** was prepared by a published procedure [2,3] with either methanol or ethanol as the solvent. Yields in ethanol are lower (60%) than those in methanol (70–80%), and up to 30% decamethylruthenocene is formed in ethanol. Upon variation of the $Ru/Cp^{\star}H$ ratio we found that a 2.5 fold excess of $Cp^{\star}H$ is necessary in order to achieve these yields. Microcrystals of **1a** obtained from the ethanol reaction are reddish brown, and are more soluble than the brownish material obtained from methanol, which probably contains a higher proportion of oligomers. The lower yields in ethanol are offset by the higher solubility of the material, and the fact that it generally gives cleaner reactions. In both cases we observed ageing of the compound during some weeks' storage at ambient temperature, the colour becoming lighter and the solubility falling. Consequently samples were stored under nitrogen at low temperatures.

$Cp^{\star}RuCl_2$ is generally described as a polymer, though its ready solubility in, e.g., CH_2Cl_2, argue against its being a high molecular weight species. Crystals were grown from a methylene-chloride solution which had been passed over silylated silica gel to remove small amounts of higher molecular weight material. Preliminary X-ray data show the structure in the solid state to be made up of dimers $(Cp^{\star}RuCl)_2(\mu\text{-}Cl)_2$, as is the analogous Rh species [16].

Treatment of **1a** with NaBr or KI in MeOH/CH_2Cl_2, evaporation of the solvent, and extraction of the residue with CH_2Cl_2 gave the bromo and iodo complexes **1b** and **1c** as dark red and violet solids, respectively, with correct elemental analyses. Like **1a**, **1b** and **1c** are readily soluble in CH_2Cl_2 and in $CHCl_3$ and slightly soluble in THF and the lower alcohols, and are formulated as dimers by analogy with **1a**.

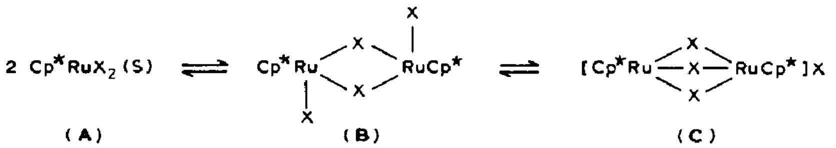
$$[Cp^{\star}RuCl_2]_2 + MX \xrightarrow[-K(Na)Cl]{MeOH/CH_2Cl_2} \begin{array}{l}[Cp^{\star}RuX_2]_2\\ (\mathbf{1b}\text{: } X = Br,\\ \ \mathbf{1c}\text{: } X = I)\end{array} \qquad (1)$$

Efforts were made to characterize the solution species by physical measurements and NMR spectra. All three halides are essentially non-conducting in halocarbon solvents, and show only very slight conductivity (Λ 5, and 9 mS) in acetonitrile and in CH_2Cl_2. **1a** is ionized water (Λ 88 mS), in which about 4×10^{-3} M solutions can be obtained, and in methanol. **1b** and **1c** are insoluble in water.

Osmometric molecular weight determination in $CHCl_3$ gave values of 500, 700, and 850 Dalton, respectively (**1a**: 614, **1b**: 792, **1c**: 962 Dalton), 10–20% lower than expected for the dimers. Though the method used is not very accurate (10–20% error) (particularly in the case of **1a**, for which the points taken at various concentrations do not fall on a straight line, indicating concentration dependent dissociation) it can be concluded that in the less polar solvents the compounds exist largely as dimers, possibly with a little dissociation into monomers.

The ion of highest mass in the mass spectra of all three halogeno complexes pertains to the fragment $(Cp^{\star}Ru)_2X_3$, followed by ions formed from this by loss of X and HX, which points to the existence of dimers in the gas phase also.

A comparison of the ^1H NMR signals of the $Cp^{\star}$ group in various solvents, shown in Table 1, is revealing. If higher oligomers are disregarded equilibria between the three forms A–C, eq. 2, must be considered:



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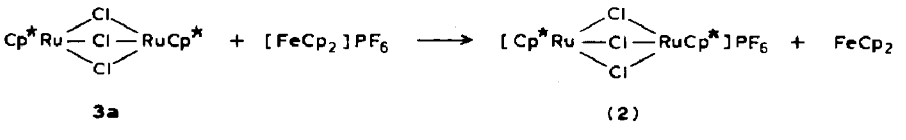


(3)

The monomeric species **A** is formed with donor ligands (see Table 1 and discussion below) and typically has a $Cp^{\star}$ signal around 15 ppm. It appears to be the dominant species in, e.g., acetonitrile . The equilibrium was locked into the ionic form **C** by oxidation of the mixed valence chloro complex **3a** (see below) with $[FeCp_2]PF_6$, eq. 3, to give the hexafluorophosphate **2**. The salt has its $Cp^{\star}$ resonance at 2.2 ppm in $CDCl_3$, practically in the diamagnetic region. The same chemical shift and narrow line width is found for the D_2O solution (solubility 4.46×10^{-3} M), suggesting ionization in water prior to hydrolysis, as observed for the analogous Rh complex [17].

The molecular dimer **B** appear to be present in solution in CH_2Cl_2. The upfield shift of the Cp* signal in chloroform then points to some participation of the ionic form **C**. In accordance with this interpretation, there is a slight upfield shift from 5.07 to 4.85 ppm when the concentration is lowered from 0.135 to 0.0168 *M*. A still higher value is found in chloroform/methanol mixtures (the solubility in pure methanol is insufficient for recording an NMR spectrum), and in THF, indicating a higher degree of ionization in these solvents. Interestingly, the heavier halide complexes show diamagnetic ^1H as well as ^{13}C NMR signals (**1b**: δ 11.92(CH_3), 104.7(C_{ipso}); **1c**: δ 12.98(CH_3), 99.01(C_{ipso})) in all non-coordinating solvents (no ^{13}C NMR signal could be obtained for **1a**). The paramangetic nature of the Ru^{III} oxidation state in these solutions shows up immediately on addition of for example, pyridine to an NMR sample, the signals being shifted downfield to the "monomeric paramagnetic" region (15–25 ppm). The variation in NMR shifts is indicative of a varying degree of coupling between the d^5-Ru^{III} centers in the dimeric molecules, obviously as a result of a superexchange process via the halide bridges, since the Ru–Ru distance is expected to increase in the sequence $Cl < Br < I$, in contrast to the decreasing paramagnetic shift in solution. Comparison of **1a** and **2** suggests that this coupling is more effective in the ionic triply-bridged than in the molecular complex.

Mixed valence $Cp^\star Ru^{III/II}$ and oligomeric $Cp^\star Ru^{II}$ halides

A general route to lower valent "ligand free" Cp*Ru halides involves the reduction of Ru^{III} halides **1** with cobaltocene. Which Cp*Ru halide is formed in the reaction depends on the molar ratio Ru/Co as well as on the halide.

With a ratio of 2/1 we obtained from **1a** an air sensitive, intense emerald green, pentane-soluble, paramagnetic compound, characterized by a broad ^1H NMR

Table 1

Cp* ^1H NMR data for the halogeno complexes $[Cp^\star RuX(\mu\text{-}X)]_2$ (**1a–1c**), $[Cp^\star Ru]_2(\mu\text{-}X)_3$ (**3a–3c**) and $[Cp^\star RuX]_n$ (**4a–4c**) (X = Cl, Br, I)

No.	solvent	δ (ppm)	$\Delta\nu$ (Hz)
1a	acetonitrile	15.2	168
	CD_2Cl_2	6.77	30
	$CDCl_3$	5.075–4.85	18
	$MeOD/CDCl_3$	3.32	37
	D_2O	2.2	sharp
1b	$CDCl_3$	1.89	sharp
1c	$CDCl_3$	1.71	sharp
2	$CDCl_3$	2.14	
3a	C_6D_6	−8.44	
3b	C_6D_6	−12.90	
3c	C_6D_6	−17.2	
4a	C_6H_{12}	1.56	
4b	C_6D_6	1.91	
4c	C_6D_6	1.79	

Table 2

^{1}H NMR data for substitution products

No.	solvent	δ
6a	CD_2Cl_2	19.06(br.s,15H,Cp*), 11.6,11.3(br.s,5H,pyridine)
6b	CD_2Cl_2	18.06(br.s,15H,Cp*), 11.65,10.15(br.s,5H,pyridine)
7	C_6D_6	18.62(br.s,15H,Cp*), 0.77(6H,acac)
8	CD_2Cl_2	1.59(s,15H,Cp*), 2.41(d,2H,*syn*), 3.99(d,2H,*anti*), 5.08(m,1H)
9a	CD_3COCD_3	2.10(2,15H,Cp*), 6.06(s,6H,Ph)
9b	CH_2Cl_2	1.84(s,15H,Cp*), 2.14(s,9H,Me), 5.39(3H,C_6H_3)
9c	$CDCl_3$	1.62(s,15H,Cp*), 2.07(s,18H,Me)
10a	CH_2Cl_2	1.61(s,15H,Cp*), 7.39(ddd,2H,H(4)), 7.70(2H,H(5), 8.00 (d,2H,H(6)), 9.22(dd,2H),H(2))
10b	CD_3COCD_3	1.60(s,15H,Cp*), 3.30(s,3H,OMe), 7.29(ddd,2H,H(4)), 7.58(2H,H(5), 8.28(d,2H,H(6), 8.83(dd,2H,H(2))
11	$CDCl_3$	1.68(s,15H,Cp*), 7.3–7.6(m,20H,Ph)
12a	CH_2Cl_2	1.15 [a](s,30H,Cp*), 3.44(m,2H,CH_2), 7.1–7.4(m,20H,Ph)
12b	C_6D_6	1.49(s,30H,Cp*), 3.18(t,H,CH_2), 3.97(s,H,OMe), 7–7.5(m,20H,Ph)
13	CH_2Cl_2	1.42(s,15H,Cp*), 2.2(m,4H,CH_2), 7.4–7.8(m,20H,Ph)
14	$CDCl_3$	1.57(s,15H,Cp*), 1.86,2.02(m,8H,CH_2), 2.54,390(m,4H,CH)
15	CD_2Cl_2	1.89(s,15H,Cp*)
16a	C_6D_6	1.62(s,15H,Cp*), 4.82(3H,OMe)
16b	C_6D_6	1.63(s,15H,CP*), 1.50(6,3H,Me), 5.01(q,2H,OCH_2)
16c	C_6D_6	1.63(s,15H,Cp*), 0.92(t,3H,Me), 1.7(m,2H,CH_2), 4.86 (t,2H,OCH_2)
16d	C_6D_6	1.64(s,15H,Cp*), 1.02(t,3H,Me), 1.82(m,4H,2CH_2), 4.97 (t,2H,OCH_2)
17	CD_2Cl_2	1.87(s,15H,CP*)

[a] Possibly in equilibrium with traces of a paramagnetic mixed valence $Ru^{II,III}$ dinuclear phosphine complex.

singlet at δ -8.4 (Table 1) and an axial EPR spectrum ($g_\parallel$ 2.067, $g_\perp$ 2.016, pentane, 14 K, Fig. 1). On the basis of its total elemental analysis (Table 3), mass spectrum (Table 4, solubility, and cleavage reactions (described below), the green compound is assigned structure **3a**.

Table 3a

Elemental analyses (found (calcd.) (%)) of Cp*Ru halogeno complexes

No.	C	H	X	Ru
1b $C_{20}H_{30}Br_4Ru_2$	30.30	3.69	Br 39.86	
	(30.32)	(3.82)	(40.34)	
1c $C_{20}H_{30}I_4Ru_2$	24.40	3.16	I51.93	
	(24.51)	(3.08)	(51.79)	
2 $C_{20}H_{30}Cl_3F_6PRu_2$	34.11	3.98		
	(33.18)	(4.18)		
3a $C_{20}H_{30}Cl_3Ru_2$	41.35	5.32	Cl 18.55	34.65
	(41.49)	(5.22)	(18.37)	(34.91)
3b $C_{20}H_{30}Br_3Ru_2$	33.65	4.11	Br 33.55	
	(33.76)	(4.22)	(33.33)	
4a $C_{10}H_{15}ClRu$ [a]	44.49	5.43	Cl 13.85	
	(44.20)	(5.56)	(13.05)	
4c $C_{10}H_{15}IRu$	33.24	4.21	I 34.79	
	(32.97)	(4.12)	(34.89)	

[a] Compound is very susceptible to oxidation and contains traces of **3a**.

Table 3b

Elemental analyses (found (calcd.) (%)) of substitution products

No.	C	H	N
6a $C_{15}H_{20}Cl_2NRu$	46.39 (46.64)	5.10 (5.22)	3.69 (3.63)
7 $C_{15}H_{22}ClO_2Ru$	48.61 (48.57)	6.12 (5.98)	
9a $C_{16}H_{21}F_6PRu$	42.60 (41.83)	4.71 (4.61)	
9b $C_{19}H_2F_6PRu$	44.95 (45.51)	5.34 (5.43)	
9c $C_{22}H_{33}F_6PRu$	48.56 (48.71)	5.90 (6.11)	
10a $C_{20}H_{23}ClN_2Ru$	55.06 (56.00)	5.41 (5.40)	6.23 (6.51)
10b $C_{21}H_{26}N_2ORu$	59.41 (59.56)	6.00 (6.19)	6.47 (6.61)
11 $C_{35}H_{37}ClP_2Ru$	64.11 (63.07)	5.80 (5.68)	
12a $C_{45}H_{52}Cl_2P_2Ru_2$	58.37 (58.25)	5.78 (5.65)	
13 $C_{36}H_{39}ClP_2Ru$	64.83 (64.52)	6.08 (5.87)	
16b $C_{24}H_{40}O_2Ru_2$	51.22 (51.22)	7.19 (7.17)	

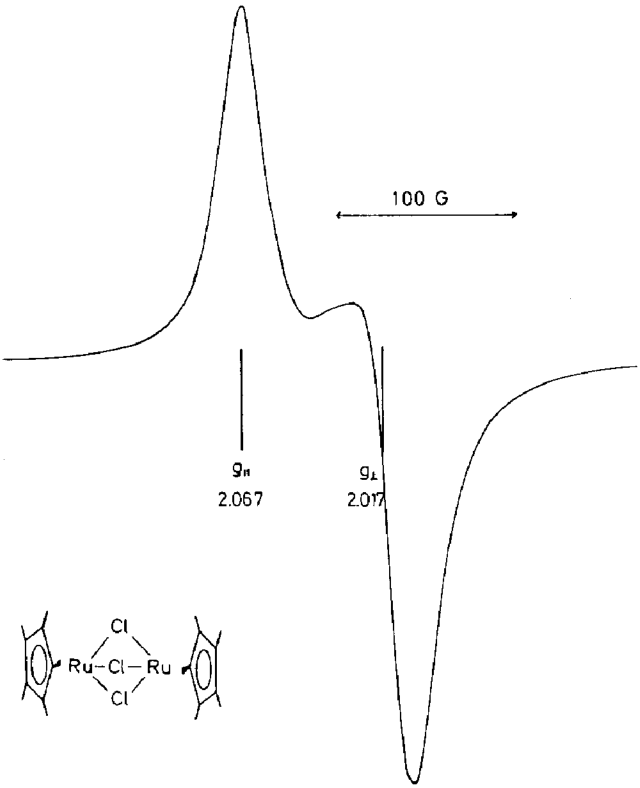


Fig. 1. X-Band EPR spectrum of **3a** in pentane, 14 K.

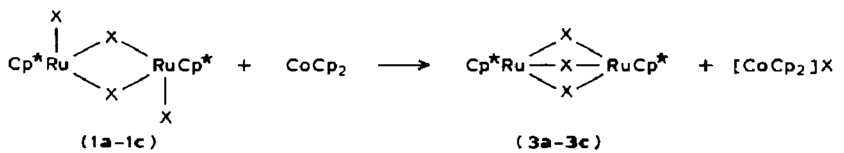
Table 4

Mass spectra of Cp*Ru complexes

No.	Fragments: m/z (based on ^{102}Ru) (I_{rel}. %, assignment)
1b	713(27,$M-\mathrm{Br}$), 633(25,$M-2\mathrm{Br}$), 397(49,$\mathrm{Cp^{\star}RuBr_2}$), 317 (100, $\mathrm{Cp^{\star}RuBr-H}$), 233(93,$\mathrm{Cp^{\star}Ru-4H = M_2-4HBr}$)
1c	4(11,$M-\mathrm{I}$), 727(52,$M-2\mathrm{I}$), 491(28,$\mathrm{Cp^{\star}RuI_2}$), 364(100,$\mathrm{Cp^{\star}Ru}$), 233(77,$\mathrm{Cp^{\star}Ru-4H = M_2-4HBr}$)
3a	578(21,$M-3\mathrm{H}$), 544(100,$M-\mathrm{Cl}$), 470(53,$\mathrm{(Cp^{\star}Ru)_2}$), 271(57,$\mathrm{Cp^{\star}RuCl-H}$), 234(82,$\mathrm{Cp^{\star}Ru-3H}$)
4a	578(24,$\mathrm{(Cp^{\star}Ru)_2Cl_3 = M_2-HCl-2H} = M'$), 544(100,$M'-\mathrm{Cl}$), 470(85,$M'-4\mathrm{HCl}$), 271(55,$\mathrm{Cp^{\star}RuCl}$), 234(90,$\mathrm{Cp^{\star}Ru-3H}$)
4c	727(100,$\mathrm{(Cp^{\star}RuI)_2}$), 600(25,$\mathrm{Cp^{\star}Ru_2I_2}$), 592(25,$\mathrm{(Cp^{\star}Ru)_2I}$), 465(15,$\mathrm{Ru_2I_2H_2}$), 460(15,$\mathrm{Cp^{\star}Ru_2I}$), 364(20,$\mathrm{Cp^{\star}RuI}$), 234($\mathrm{Cp^{\star}Ru-3H}$)
5c	similar to **3a**, no fragments containing Ru and $\mathrm{PPh_3}$
6a	similar to **3a**, in addition 361(5,$\mathrm{Cp^{\star}Ru(pyr)Cl}$
7	370(35,$M-\mathrm{H}$), 335(100,$M-\mathrm{HCl}$), 233(100,$\mathrm{Cp^{\star}Ru-4H}$), 201(30,Ru(acac))
10a	428(100,M), 392(75,$M-\mathrm{HCl}$), 271(35,$\mathrm{Cp^{\star}RuCl}$), 236(100,$\mathrm{Cp^{\star}Ru-H}$)
10b	392(15,$M-\mathrm{MeOH}$), 234(10,$\mathrm{Cp^{\star}Ru-3H}$), 156(100,bipy)
11	656(100,M), 621(40,$M-\mathrm{Cl}$), 435(74,$\mathrm{Cp^{\star}RuPPh_2CH}$), 420(33,$\mathrm{Cp^{\star}RuPPh_2-2H}$), 233(48,$\mathrm{Cp^{\star}Ru-4H}$)
12a	928(10,M), 656(100,$\mathrm{Cp^{\star}Ru(PPh_2)_2CH_2Cl}$), 621(74,$\mathrm{CP^{\star}Ru(PPh_2)_2CH_2}$), 435(70,$\mathrm{PPh_2CH}$), 420(13,$\mathrm{CP^{\star}RuPPh_2-2H}$)
12b	920(15,M), 889(25,$M-\mathrm{OMe}$), 858(20,$M-2\mathrm{MeOH}$), 812(35,$M-\mathrm{MeOH-PhH}$), 781(35,$\mathrm{(Cp^{\star}Ru)_2P_2Ph_3CH_2}$), 735(15,$\mathrm{(Cp^{\star}RuOMe)_2PPh_2CH_2}$), 704($\mathrm{Cp^{\star}RuOMeCp^{\star}Ru}$-$\mathrm{PPh_2CH_2}$), 625(15,$\mathrm{Cp^{\star}RuOMePPh_2CH_2}$), 621(100,$\mathrm{Cp^{\star}Ru(PPh_2)_2CH_2}$), 498-(95,$\mathrm{Cp^{\star}RuOMePPh_2CH_2}$), 467(95,$\mathrm{Cp^{\star}RuPPh_2CH_2}$), 436(60,$\mathrm{Cp^{\star}RuPPh_2C}$), 422(90, $\mathrm{Cp^{\star}RuPPh_2}$).
13	670(100,M), 633(18,$M-\mathrm{HCl-H}$)

Analogous compounds **3b** (blue green) and **3c** (violet) were formed by the halogeno complexes **1b** and **1c**. Though triply-bridged mixed-valence Ru$^{\mathrm{II/III}}$ complexes are encountered in the coordination chemistry of ruthenium [18,19]; compounds **3** appear to be the first organometallic examples of this type.

The reduction cannot be controlled entirely by the stoichiometry. Complexes $[\mathrm{Cp^{\star}RuX}]_n$ (**4**) are also formed through reaction 5, in an increasing proportion on going from Cl to I. Thus yields of **3** drop from 60% in the case of **3a**, through 20%



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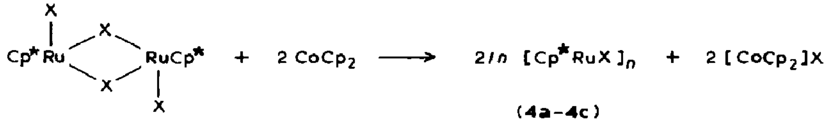

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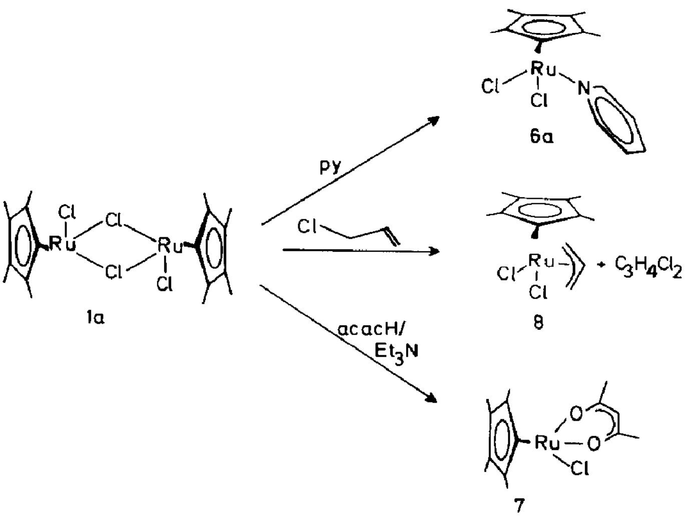
(a : X = Cl , b : X = Br , c : X = I)



Scheme 1.

for **3b**, to about 10% for **3c**. The latter compound was identified by its characteristic high field ^{1}H NMR resonance (Table 1). The presence of decamethylruthenocene (δ 1.64 ppm), in varying amounts, was also evident from the NMR spectra.

Purification of the mixed valence complexes **3a** and **3b** was achieved by repeated precipitation by cooling their solutions in pentane, in which the by-products are more soluble. Neither of the complexes **3** was stable to chromatography on alumina or silica. The species $[\text{CpRuCl}]_n$ (**4a**) could be separated from the mixture obtained by reduction of **1a** by chromatographing the pentane solution on finely powdered $MgSO_4$ [20*]. The more readily soluble complex **4a** is eluted first and can be obtained free from **3a**, but the latter could not be obtained pure in this way.

An easier route to **3a** was through comproportionation of **4a** with **1a** in pentane/THF, as in eq. 6. The equilibrium 6 lies to the right in solvents in which the components are of comparable solubility. In pentane, in which **1a** is insoluble, the Ru$^{\text{III}}$ complex tends to separate from solution.

$$\underset{\textbf{(1a)}}{(\text{Cp}^\star\text{RuCl})_2(\mu\text{-Cl})_2} + 2/n\underset{\textbf{(4a)}}{(\text{Cp}^\star\text{RuCl})_n} \rightleftarrows \underset{\textbf{(3a)}}{2\text{Cp}^\star\text{Ru}(\mu\text{-Cl})_3\text{RuCp}^\star} \qquad (6)$$

Green mixed valence complexes of type **3** with various bridging anions have frequently been identified through the mass spectra of the products of reactions such as the attempted dehalogenation of **1a** with silver salts($AgOOCH_3$, $AgOOCF_3$, $AgBF_4$) or treatment of it with a base.

Cleavage of 1a, complexes Cp**Ru*^{III}*LCl*$_2$

Cleavage reactions of **1a** to afford paramagnetic derivatives $\text{Cp}^\star\text{RuLX}_2$ are outlined in Scheme 1. The formation of the complex $\text{Cp}^\star\text{RuCl}_2\text{PPh}_3$ (**5**) [6] in the reaction with PPh_3 is indicated by (a) appearance in the ^{1}H NMR spectrum of a broad signal at 24.5 ppm for Cp* and broadened signals at 9.53, 8.60 and 6.78 ppm

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* Reference number with asterisk indicates a note in the list of references.

($CDCl_3$) assigned to Ph protons and (b) by the cyclovoltammogram [21] of **1a** in CH_2Cl_2 in the presence of PPh_3, which shows an irreversible reduction wave at −0.45 V (vs. SCE) not present for the pure halide complex, but attempted purification by chromatography resulted in partial decomposition.

An isolable Ru^{III} complex of the above type was obtained by treating **1a** with an excess of pyridine. The sparingly soluble red compound $Cp^{\star}RuCl_2(C_5H_5N)$ (**6a**) has a broad ^1H NMR ($Cp^{\star}$) signal at 19 ppm and resonances due to pyridine protons around 11 ppm (Table 2). The formation of an analogous bromo-complex $Cp^{\star}RuBr_2(C_5H_5N)$ (**6b**) was observed from the NMR spectrum (Table 2) on addition of pyridine to the solution of **1b** in CD_2Cl_2, but it could not be isolated.

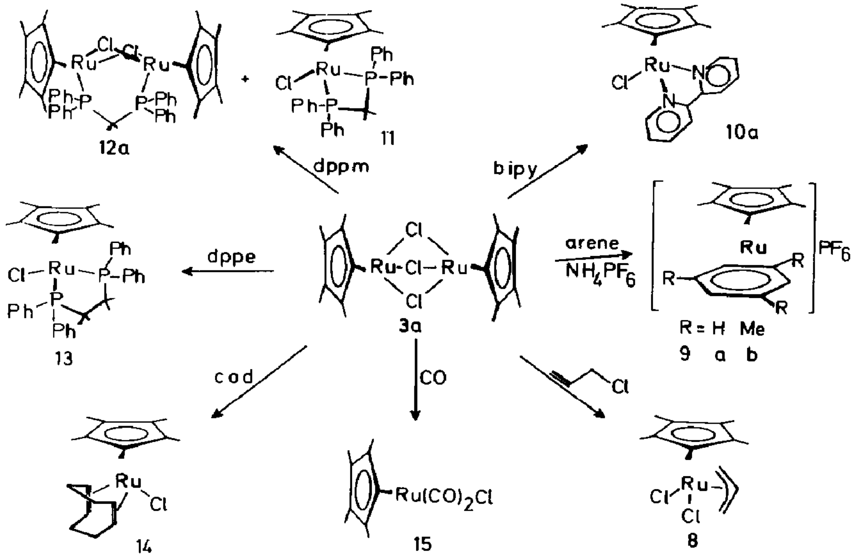
Another Ru^{III} derivative characterized was the brown red acetylacetonate $Cp^{\star}Ru(acac)Cl$ (acac = η^2-$C_3H_5O_2$) (**7**) with a $Cp^{\star}$ resonance at 18.6 ppm, which was formed when **1a** was treated with acacH in the presence of triethylamine.

Finally we note that reaction of **1a** with allyl-chloride, which was previously reported to give the complex $Cp^{\star}Ru(\pi\text{-allyl})Cl_2$ (**8**) [10] in ethanol, yields the same products in dichloromethane, i.e. in the absence of a reductant; 1,3- or 2,3-dichloropropene was identified as the by-product by GC/MS. This product may be formed by chlorination of excess allyl-chloride by an intermediate complex $Cp^{\star}RuCl_3(C_3H_5)$.

The above reactions suggest that the $Cp^{\star}Ru^{III}$ moiety is stabilized mainly by donor ligands, and becomes a fairly strong oxidant when bearing acceptor ligands; this conclusion was fully substantiated by electroanalytical measurements [21].

Cleavage reactions of 3a

The mixed valence complex **3a** was characterized by a number of cleavage reactions summarized in Scheme 2. In most instances the disproportionation took place readily on addition of the two- or four-electron ligands. Only the formation of the arene complexes **9** needed longer reaction times or more forcing conditions. As



Scheme 2.

generally observed for formation of these sandwich compounds, complexation is more difficult the more methylated is the arene ligand [22]. Thus, **3a** gave no complex with hexamethylbenzene.

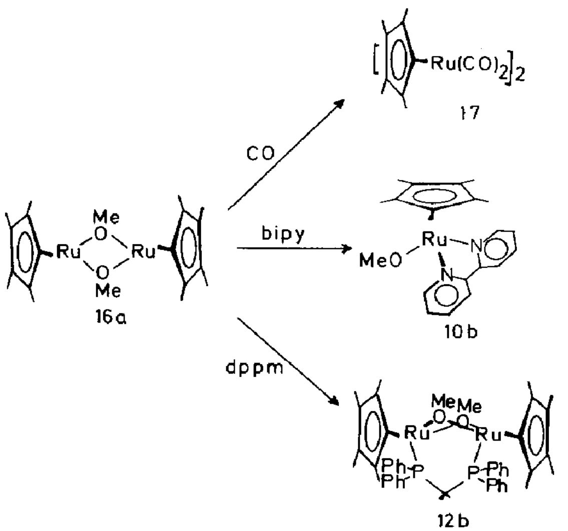
For reasons differing from case to case, in all the reactions shown in Scheme 2 only the Ru^{II} part of **3a** was transformed into an isolated and characterized complex. In reactions with the arenes cyclooctadiene or CO, the Ru^{III} part is left as **1a**. Yields in these cases never exceeded 50% based on total Ru.

The diphosphines gave ionic or oligomeric Ru^{III} phosphine complexes that are difficult to isolate in pure form, and so the ether insoluble part of the reaction mixture was not further investigated. The same holds for the cleavage reaction of **4a** with bipyridine. The presence of an ionic bipyridineruthenium(III) complex, [Cp*Ru(bipy)Cl]Cl, the product of the reaction of **1a** with bipyridine, can be proved electrochemically [21] but the compound has never been isolated pure. The Ru^{II} complex **10a**, which dissolves in ether, was isolated and purified. The same compound was obtained from **4a** and bipyridine (see Scheme 4).

The reaction with allyl chloride involves oxidative addition to Ru^{II} to give the allylruthenium(IV) complex directly whereas the Ru^{III} part may react as indicated above. The yield in this instance is significantly above 50%, indicating a stoichiometry which includes the Ru^{III} part.

*Alkoxo complexes [Cp*RuOR]$_n$ (16)*

The halide complex **1a**, was found to be readily reduced in methanol in the presence of bases such as hydroxide, acetate, fluoride or carbonate. A dilute (10^{-4} *M*) solution in dry methanol turned green within an hour at ambient temperature indicating the formation of the mixed valence complex **3a**. In the absence of added base the reduction stops at this stage. If the mixture is then stirred over solid K_2CO_3 the reaction proceeds further, giving a dark red (λ_{max} 508 nm), highly air-sensitive solution, from which (Cp*RuOMe)$_2$ (**16a**) can be isolated by extraction with pentane or ether in nearly quantitative yield [1], **16a** is readily soluble in non-polar media, but tends to react with halocarbon and aromatic solvents.



Scheme 3.

The higher homologues up to R = Bu^n, were obtained similarly. In the reaction with ethanol an $\text{Cp}^\star$Ru ethoxy complex of higher nuclearity was formed in addition to **16b** but could not be isolated pure. Yields fall with increasing hydrocarbon chain length. No alkoxo complexes were obtained with tertiary alcohols.

$$(\text{Cp}^\star\text{RuCl}_2)_2 + 3\ \text{ROH} + 4\ \text{OH}^- \rightarrow (\text{Cp}^\star\text{RuOR})_2 + \text{CH}_2\text{O}\ [25] + 2\ \text{H}_2\text{O} + 4\ \text{Cl}^-$$

$$\begin{array}{l}(\textbf{16a}\text{: R = Me;}\\ \textbf{16b}\text{: R = Et;}\\ \textbf{16c}\text{: R = Pr}^n\text{;}\\ \textbf{16d}\text{: R = Bu}^n\text{)}\end{array} \qquad (7)$$

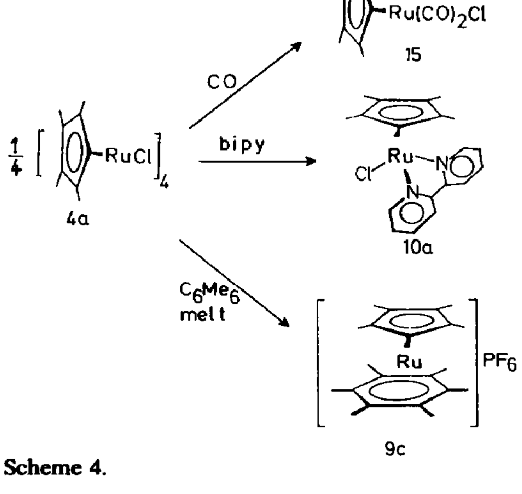
On addition of two- or four-electron ligands to **16a**, complexes $\text{Cp}^\star\text{RuL}_2\text{OMe}$ (see Scheme 3) were preferentially formed. To obtain the bipyridine complex **10b** it is necessary to avoid an excess of bipyridine which will complex with the metal to give $\text{Ru(bipy)}_2(\text{OMe})_2$. When CO was bubbled through the solution at ambient temperature for 5 min, the dimeric carbonyl **17** was formed surprisingly. The fate of the methoxy group in this reaction is not clear.

The synthetic potential of the alkoxo complexes **16** is widened because of their reactions with electrophiles such as that with Me_3SiCl, eq. 8, which makes the chloro complex **4a** a readily available synthon.

$$\underset{(\textbf{16})}{(\text{Cp}^\star\text{RuOR})_2} + 2\ \text{Me}_3\text{SiCl} \rightarrow 2/n\underset{(\textbf{4a})}{(\text{Cp}^\star\text{RuCl})_n} + 2\ \text{Me}_3\text{SiOR} \qquad (8)$$

The complexation reactions outlined in Scheme 4 were performed as an initial probe of the synthetic use of this coordinatively unsaturated halide. Most notable of its reactions is the reaction with hexamethylbenzene, conducted in a melt of C_6Me_6 at 160 °C, to give the permethylated cyclopentadienyl(arene)ruthenium cation **9c**, which had not been obtained by complexation of the mixed valence complex **3a**.

The reactions described above are illustrative of the broad synthetic potential of halides and alkoxides of the $\text{Cp}^\star$Ru moiety. The complexation reactions proceed



Scheme 4.

more readily the lower the Ru oxidation state in the oligomeric unit. In particular, the Ru^{II} complexes $[Cp^{\star}RuX]_n$, where X is halide or alkoxide, can be used as starting materials for the preparation of any conceivable $Cp^{\star}RuL_2X$ compound.

Experimental

All reactions were conducted under purified nitrogen in anhydrous solvents saturated with nitrogen. Spectrometers were Bruker SY 80 (80 MHz) and WH 270 (270 MHz) for NMR, Perkin–Elmer 580 for IR, Varian CH5 DF for MS. Conductivities were measured with a WTW-Weilheim AC bridge. Molecular weights were determined with a Knauer vapor pressure osmometer. Microanalyses were by the microanalytical laboratories, Engelskirchen, or the microanalytical laboratory of the institute.

Molar quantities of polynuclear complexes below refer to the monomeric molecular unit.

Bis(pentamethylcyclopentadienyl(μ-bromo)ruthenium bromide), $[Cp^{\star}Ru(\mu\text{-}Br)Br]_2$ *(1b).* Sodium bromide (30 g, 29 mmol) was added to a solution of **1a** (1.0 g, 3.2 mmol) in 20 ml of 1/1 $MeOH/CH_2Cl_2$. The mixture was stirred for 1 h, during which the colour changed from brown to dark red. The solvent was evaporated, the residue extracted with CH_2Cl_2, the extract filtered and evaporated to small volume, and the product precipitated by addition of ether. Decantation of the mother liquor and washing the residue twice with ether left 1.2 g (93%) of dark-red microcrystals.

Bis(pentamethylcyclopentadienyl(μ-iodo)ruthenium iodide), $[Cp^{\star}Ru(\mu\text{-}I)I]_2$ *(1c).* A similar procedure gave **1c**. Yield 95%.

Tri-μ-chloro bis(pentamethylcyclopentadienylruthenium(III,III)) hexafluorophosphate, $[(Cp^{\star}Ru)_2(\mu\text{-}Cl)_3]PF_6$ *(2).* To 0.3 g (1 mmol) of **4a** was added 0.31 g (1 mmol) $[FeCp_2]PF_6$ in 20 ml of CH_2Cl_2. When the mixture was stirred the colour changed from green to brown. Pentane was added and the solution set aside at 0 °C for 24 h. Decantation left a brown solid, which was washed twice with ether and dried. Yield 80%.

Tri-μ-chloro bis(pentamethylcyclopentadienylruthenium(II,III)), $Cp^{\star}Ru(\mu\text{-}Cl)_3RuCp^{\star}$ *(3a).* (a) By reduction of **1a** with $CoCp_2$: To a suspension of 1.0 g (3.2 mmol) of **1a** in 20 ml of THF was added 0.3 g (1.58 mmol) of freshly sublimed cobaltocene. On complete dissolution of the Ru complex the mixture turned green. After 15 min stirring the solvent was evaporated, the residue was dissolved in ether and the solution was filtered and evaporated to dryness. The residual solid was treated with 30 ml of pentane, in which it is moderately soluble. The intense green pentane solution was transferred by canulous to a second Schlenk tube. The solution was cooled by evaporating part of the solvent under a water-pump vacuum, and most of the material precipitated. The mother liquor was decanted and the procedure repeated with another 30 ml of pentane. Finally the product was dried under vacuum, leaving 560 mg (60%) of a dark green microcrystalline powder.

(b) By comproportionation of **1a** and **4a**: A solution of about 1 mmol **4a** in 50 ml ether was added to 1.5 mmol of **1a** suspended in THF and the mixture stirred for 1 h. The solvent was then evaporated, the residue was extracted with pentane (which left unchanged **1a**) and the saturated extract was cooled to −30 °C to give the product in nearly quantitative yield.

*Tri-μ-bromo-bis(pentamethylcyclopentadienylruthenium(II,III)), $Cp^{\star}Ru(\mu\text{-}Br)_3Ru\text{-}Cp^{\star}$ (**3b**).* The procedure was analogous to that in method (a) for **3a**. The product is turquois. The yield was 225 mg (25%).

*Chloro(pentamethylcyclopentadienyl)ruthenium(II), $[Cp^{\star}RuCl]_n$, (**4a**) [1].* To a solution of **16a** in pentane or ether was added a slight excess of Me_3SiCl which had been distilled from K_2CO_3. An immediate colour change from red to brown indicated the formation of the product. The solvent was evaporated and the residue dried under vacuum to remove Me_3SiOMe and excess Me_3SiCl and leave **4a** in quantitative yield. The material obtained in this way is pure enough for use in further reactions. It can be recrystallized from ether to give orange yellow crystals.

*Iodo(pentamethylcyclopentadienyl)ruthenium(II), $[Cp^{\star}RuI]_n$ (**4c**).* To a suspension of 0.5 g (1.0 mmol) of **1c** in 20 ml of THF was added 0.19 g (1.0 mmol) of $CoCp_2$. The dark red solution was stirred for 15 min, the solvent was evaporated and the residue extracted twice with 20 ml pentane. Some pentane was evaporated from the extract without heating, and the remainder was decanted when the dark-red solid had separated. Drying under vacuum left 360 mg (50%) of dark microcrystals.

*Dichloro(pentamethylcyclopentadienyl)(pyridine)ruthenium(III), $Cp^{\star}Ru(C_5H_5N)Cl_2$ (**6a**).* To 0.5 g (1.6 mmol) of **1a** in 20 ml of CH_2Cl_2 was added 0.26 g (3.3 mmol) of pyridine. The colour changed from brown to red within 2 h. The solvent and residual pyridine were evaporated and the residue was redissolved in CH_2Cl_2. The solution was filtered. Crystallization was achieved by addition of pentane and cooling, to give 555 mg (90%) of red crystals, which were rapidly dried under vacuum , since otherwise the complex loses pyridine.

Chloro(η^2-2,4-pentanedionato)(pentamethylcyclopentadienyl)ruthenium(III), $Cp^{\star}\text{-}RuCl(C_5H_7O_2)$ (7). To a stirred solution of 0.36 g (1.07 mmol) of **1a** in 20 ml of CH_2Cl_2 was added 0.22 g (2.16 mmol) of acetylacetone followed by 0.1 g (1.5 mmol) of triethylamine. After 3 h stirring at room temperature the solvent was evaporated and the residue extracted three times with 20 ml of pentane. The extract was evaporated to leave a red solid. Yield 85%.

Reaction of 1a and of 3a with allyl chloride

π-Allyl(dichloro)(pentamethylcyclopentadienyl)ruthenium(IV), $Cp^{\star}RuCl_2(\eta^3\text{-}C_3H_5)$ (8). (a) By reaction of **1a** with allyl chloride: A solution of 0.31 g (1.0 mmol) of **1a** and 0.8 g (10.5 mmol) of allyl chloride in CH_2Cl_2 was stirred for 6 h at ambient temperature. The colour changes from brown to dark orange. The solvent and the excess of allyl chloride were evaporated off, and the residue was redissolved in CH_2Cl_2. The solution was filtered and the product crystallized by addition of pentane. The red crystals lose CH_2Cl_2 when dried under high vacuum and become orange. Yield was 0.28 g (80%). Spectra and analytical data were in agreement with those reported in ref. 10.

(b) From **3a** and allyl chloride: On addition of 0.3 g (4.2 mmol) of allyl chloride to 0.49 g (0.8 mmol) of **4a** in 20 ml of pentane an immediate colour change and separation of an orange solid were observed. Decantation and work-up of the product as described above gave **8** in 85% yield.

*Benzene(pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate, $[Cp^{\star}Ru\text{-}(C_6H_6)]PF_6$ (**9a**) [26].* To 0.4 g (0.66 mmol) of **3a** in 20 ml benzene was added 100 mg of $AlCl_3$. The mixture was stirred for 2 h at ambient temperature. The solvent was decanted from the brown solid, which was dissolved in water. The solution was filtered and the product precipitated by addition of NH_4PF_6. Reprecipitation from CH_2Cl_2/ether gave pure product. Yield 50%.

Mesitylene(pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate, [Cp-Ru($C_6H_3Me_3$)]PF_6 (**9b**) [26].* This was made as described for **9a**, but stirring for 24 h was necessary for completion of the reaction. Yield 50%.

*Hexamethylbenzene(pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate, Cp*Ru(C_6Me_6)PF_6 (**9c**) [26].* A mixture of **4a** (0.32 g, 1.3 mmol Ru) with a five-fold excess of hexamethylbenzene was heated to 165 °C to melt the solid and then cooled. The excess of hexamethylbenzene was removed by two extractions with pentane, the residual solid dissolved in water, and the complex salt precipitated as the PF_6 salt. Purification was as described for **9a** and **9b**. Yield 55%.

*Bipyridinechloro(pentamethylcyclopentadienyl)ruthenium(II) (**10a**).* (a) From **4a**. To a solution of **4a** (0.32 g, 1.3 mmol Ru) in 120 ml of pentane was added 0.203 mg (1.3 mmol) 2.2′-bipyridine. Within minutes the mixture turned to dark violet. After 1 h stirring the solvent was evaporated and the residue washed with several small portions of ether to remove the excess of bipyridine. The residue was dried, then dissolved in the minimum quantity of acetone, and ether was added until the solution became slightly turbid. The product was allowed to crystallize out overnight at −30 °C, the mother liquid decanted, and the residue again washed with ether. Yield 70%.

(b) From **3a**: the procedure was similar to that described above. Yield 75%.

10a appears to be somewhat unstable, particularly in solution. Thus the elemental analysis gave a C content slightly below and a N content slightly above the calculated value.

Cleavage of 3a with bis(diphenylphosphino)methane

*Chloro(bis(diphenylphosphino)methane)(pentamethylcyclopentadienyl)ruthenium(II), Cp*RuCl(η^2-($Ph_2P)_2CH_2$) (**11**) and bis(pentamethylcyclopentadienyl)di-μ-chloro-μ-bis(diphenylphosphino)methane)diruthenium, (Cp*Ru$)_2(\mu$-Cl$)_2(\mu$-($Ph_2P)_2CH_2$ (**12a**).* To 0.4 g (0.66 mmol) of **3a** in 20 ml pentane, a solution of 0.3 g (0.7 mmol) of bis(diphenylphosphino)methane in 20 ml of ether was added in portions. The reaction was indicated by a colour change from green to dark orange and separation of a brown solid. The solution was filtered, then evaporated without heating. The orange precipitate which separated was rapidly filtered off, leaving a red mother liquor. The orange solid after washing with pentane was found to be analytically pure **11** (15%). When the red mother liquor was kept at −30 °C, **12a** separated as red crystals in 30% yield.

Cleavage of 3a with bis(diphenylphosphino)ethane

*Chloro(bis(diphenylphosphino)ethane)(pentamethylcyclopentadienyl)ruthenium(II), Cp*RuCl(η^2-($Ph_2P)_2C_2H_4$) (**13**).* To 0.4 g (0.66 mmol) of **3a** in 20 ml ether was added 0.6 g (1.5 mmol) of bis(diphenylphosphino) ethane. The color changed to orange. After 15 min stirring the ether solution was decanted from the dark residue ([Cp*RudppeCl]Cl) and the solvent evaporated to yield the product, which was purified by chromatography on alumina (4% water) with pentane/ether as eluent. The yield was 0.13 g (60%, based on the stoichiometry of the reaction).

*Cleavage of **3a** with cyclooctadiene*

*1,5-Cyclooctadiene(pentamethylcyclopentadienyl)chlororuthenium(II) Cp*Ru(η^4-1,5-C_8H_{12})Cl (**14**).* To 0.4 g (0.66 mmol) of **3a** in 20 ml of ether was added 1 ml 1,5-cyclooctadiene. The green colour changed to orange within a few minutes and a dark solid separated (Cp*$RuCl_2$). After 1 h stirring the solution was filtered and the filtrate evaporated. The orange solid was chromatographed on alumina with CH_2Cl_2/ether as eluent. Yield 60%. Analytical and spectral data were in accord with those in ref. 3.

*Cleavage of **3a** with CO*

*Dicarbonyl(pentamethylcyclopentadieyl)chlororuthenium(II), Cp*Ru(CO)$_2$Cl **15** [23].* Carbon monoxide was bubbled for 5 min into a solution of 0.5 g (0.82 mmol) of **3a** in 20 ml of pentane. The solution turned yellow and **1a** separated as a brown solid. The pentane solution containing **15** was decanted and the solid chromatographed on alumina with pentane/ether as eluent and finally crystallized from pentane/ether. Yield 50%.

The complex was also obtained in high yield by bubbling CO through a pentane solution of **4a**, and isolated as described above.

*Bis(pentamethylcyclopentadienyl)methoxoruthenium(II), (Cp*RuOMe)$_2$, (**16a**).* To a solution of 0.5 g (1.6 mmol) of **1a** dissolved in 20 ml of MeOH was added 2 g K_2CO_3 (which had been dried at 200 °C). The mixture was either stirred for 6 h at room temperature or refluxed for 0.5 h, after this period it had turned dark red. The solvent was evaporated and the residue extracted repeatedly with pentane, or with ether in the case of larger batches. (After exhaustive extraction the remaining solid was white). The extract was filtered, then evaporated to give a dark red, air-sensitive solid in essentially quantitative yield. The product was recrystallized by cooling a concentrated pentane solution. **16a** is soluble in all solvents but reacts with halocarbons such as $CHCl_3$. Spectral and analytical data were as in ref. 1.

*Bis(pentamethylcyclopentadienyl)ethoxoruthenium(II), (Cp*RuOEt)$_2$, (**16b**).* This was prepared in the same way as **16a**. Yield 25%. The properties of **16b** are similar to those of **16a**. Complexes **16c** ($R = Pr^n$) and **16d** ($R = Bu^n$) were isolated in low yield and characterized by ^1H NMR and mass spectroscopy.

*Chloro(pentamethylcyclopentadienyl)ruthenium(II), [Cp*RuCl]$_n$ (**4a**).* To a pentane or ether solution of **16a** was added a slight excess of Me_3SiCl which had been distilled over K_2CO_3. An immediate colour change to brownish yellow indicated the conversion of **16a** into **4a**. The yield was quantitative. The product was recrystallized by cooling a pentane solution to −30 °C.

*Cleavage of **16a** with bipyridine*

*Bipyridinemethoxy(pentamethylcyclopentadienyl)ruthenium(II) (**10b**).* The residue left after evaporation of the solvent in the preparation of **16a** (see above), containing 0.27 g (1 mmol) of **16a**, was dissolved in 50 ml ether and 156 mg (1 mmol) of 2,2′-bipyridine was added. A slow colour change and the precipitation of a brownish-green solid took place when the mixture was stirred at ambient temperature. After 1 h the solid was filtered off, washed with ether, and dried. Yield 85%.

*Cleavage of **16a** with CO*

*Bis(dicarbonyl(pentamethylcyclopentadienyl)ruthenium(I) (**17**) [24].* A slow stream of CO was bubbled for 5 min through a solution of 0.2 g (0.75 mmol) **16a** in

30 ml of pentane. The solution turned reddish brown and a dark solid separated. The solution contained a mixture of carbonyls which were not separated. The dark solid was dissolved in dichloromethane, and **17** precipitated in 70% yield by addition of pentane.

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