

Cyclopentadienylruthenium complexes with sulphur donor ligands

II *. A comparative study of the reactivity of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{L})_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$; $\text{L} = \text{CO},$ $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2/2, \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$) towards anionic (S–S) donor ligands

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Abstract

The complexes $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) readily react with the tertiary phosphines $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) and $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (tcep) to give $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{dppe})$ and $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{tcep})_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$). The dppe complex with $\text{R} = \text{CH}_3$ reacts with $(\text{S}_2\text{COR}')^-$ ions to give $\text{Ru}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{S}_2\text{COR}')(\text{dppe})$ ($\text{R}' = \text{Me}, \text{Et}$) involving monodentate coordination of the dithiolate, and with $(\text{S}_2\text{CNR}'_2)^-$ ions to give $\text{Ru}(\text{S}_2\text{CNR}'_2)_2(\text{dppe})$ ($\text{R}' = \text{Et}$). The tcep complexes do not react with the dithiolates under these conditions. The reaction of $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$ with KS_2COEt has also been studied.

Introduction

Reactions of $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ with a variety of neutral nucleophiles take place by replacement of one or both triphenylphosphine ligands and formation of neutral complexes [2] or by displacement of chloride to give cationic species [3]. The ready replacement of the chloride ligand in $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ arises from the lability of the Ru–Cl bond and is in contrast to the behaviour of $\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$ [4].

* For Part I see ref. 1.

The two triphenylphosphine ligands of the $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ complex are readily displaced by chelating bisphosphines such as dppe or dppm [2]. With chiral diphosphines, chiral complexes are formed; in these complexes the chiral centers are located on the metal or on the diphosphine ligands, and various diastereoisomers can be separated [5].

The reactions of $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{L})_2$ ($\text{L} \neq \text{PPh}_3$) have previously received little attention, in contrast to those of the analogous iron complexes (6,7).

Because of the great interest in the chemistry of dithiolate ligands such as xanthates or dithiocarbamates [8], we previously carried out [1] the synthesis of several cyclopentadienyl dithiolate complexes of ruthenium(II) by reaction of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) and the anionic (S-S) donor ligands MS_2CX ($\text{M} = \text{Na}, \text{K}, \text{NH}_4$; $\text{X} = \text{OR}', \text{NR}'_2, \text{CN}$). However, there have been no previous reports on $\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{S-S})(\text{CO})_n$ ($n = 1, 2$) complexes, though the analogous iron complexes have been described [9,10]. The monodentate complex $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CNEt}_2)(\text{CO})_2$ is easily synthesised [10,11], but the displacement of one carbonyl group with chelation of the dithiocarbamate ligand is a difficult process [11] that can be induced by several reagents [9].

We now describe the preparation of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{L})_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$; $\text{L} = \text{dppe}/2, \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (tcep)) by the replacement of the PPh_3 ligands, and study the reactions of these complexes with dithiolate ligands and compare them with the similar reactions of $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$.

Results and discussion

Reactions with phosphines

Prolonged heating of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) with an equivalent of dppe in toluene gives the complexes $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{dppe})$ ($\text{R} = \text{H}$ (I), CH_3 (II), CH_3CO (III)). Their IR and ^1H NMR spectra (Table 1) are similar to those of the analogous triphenylphosphine complexes, suggesting that there is a similar environment around the metal.

Complexes II and III show two signals for the cyclopentadienyl protons. Analogous to the assignments made for the triphenylphosphine complexes, we assigned the signal at the higher field to protons 3 and 4 and the signal at lower field to protons 2 and 5 [1].

The reaction of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ with an excess of tcep in toluene gives $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{tcep})_2$ ($\text{R} = \text{H}$ (IV), CH_3 (V), CH_3CO (VI)). The spectral data (Table 1) show that both PPh_3 ligands have been replaced and the $\nu(\text{CN})$ band corresponding to the nitrile groups indicates that the tcep ligand acts only as a P donor. The same reaction in acetone solution also gives complexes IV-VI, which remain in solution. Thus we attribute the ease of substitution of the PPh_3 groups by the less basic tcep [12] to the nucleophilic character of the metal in $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ rather than to the insolubility of the tcep complexes in the reaction in toluene.

The ^{31}P NMR spectra of complexes II and V and the analogous complex with PPh_3 (Table 2) show that in all cases two phosphorus atoms are equivalent, which confirms the proposed bonding mode of the phosphines; the δ values are consistent with the donor abilities of the phosphine ligands.

As Haines and du Preez observed for polar solvents [4], the values of the molar conductivities of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{L})_2$ ($\text{L} = \text{PPh}_3, \text{dppe}/2$) in acetonitrile solution

Table 1
Analytical and spectral data for the complexes

Complex	Colour	Yield (%)	Analyses ((Found (calcd.) (%))			IR data (cm ⁻¹)		¹ H NMR data (δ (ppm)) ^a							
			C	H	N	ν(Ru-Cl)	ν(C-O) xant	Ph	Cp	k-Cp	others				
Ru(η-C ₅ H ₅)Cl(dppe) (I)	Yellow	75	62.48 (62.05)	5.12 (5.04)		285w		7.6-7.1m	4.55s		2.50m	P-CH ₂			
Ru(η-CH ₃ C ₅ H ₄)Cl(dppe) (II)	Orange	82	63.01 (62.59)	5.19 (5.25)		285w		7.6-7.2m	3.97m	3.30m	1.97s	2.7-2.5m	P-CH ₂		
Ru(η-CH ₃ COC ₂ H ₄)Cl(dppe) (III)	Orange	61	60.26 (61.73)	5.14 (5.02)		280w		7.7-7.1m	5.31m	4.14m	1.95s	2.70m	2.23m	P-CH ₂	
Ru(η-C ₅ H ₅)Cl(tcep) ₂ (IV)	Yellow	74	45.87 (46.98)	5.06 (4.97)	15.11 (14.29)	300m					4.95s ^b	2.65m	P-CH ₂		
Ru(η-CH ₃ C ₅ H ₄)Cl(tcep) ₂ (V)	Yellow	79	46.42 (47.88)	5.21 (5.19)	13.68 (13.95)	200w					4.43m	3.43m ^b	1.93s	2.37m	CH ₂ -CN
Ru(η-CH ₃ COC ₂ H ₄)Cl(tcep) ₂ (VI)	Orange	52	45.97 (47.66)	5.12 (4.96)	13.73 (13.34)	275w					5.26m	4.30m ^b	2.00s	2.8-2.1m	P-CH ₂
Ru(η-CH ₃ C ₅ H ₄)S ₂ COCH ₃ (dppe) (VII)	Yellow	56	58.71 (59.55)	5.44 (5.00)			1110s, 1200s	7.7-7.1m	4.62m	4.10m	1.90s	2.5-2.3m	P-CH ₂		
Ru(η-CH ₃ C ₅ H ₄)S ₂ COC ₂ H ₅ (dppe) (VIII)	Yellow	59	59.16 (60.07)	5.28 (5.19)			1120s, 1180s	7.6-7.0m	4.76	4.20m	1.93s	2.6-2.2m	P-CH ₂		
Ru(η-C ₅ H ₅)S ₂ COC ₂ H ₅ (CO) (IX)	Yellow	41	35.16 (34.28)	3.44 (3.20)			1230s				1040m				
Ru(S ₂ CN(C ₂ H ₅) ₂) ₂ (dppe)	Yellow	-	55.01 (54.32)	5.55 (5.57)	3.48 (3.52)						1945s				

^a In CDCl₃ except where otherwise stated, with TMS as internal standard. ^b In CD₃COCD₃.

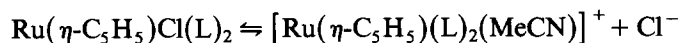
Table 2

³¹P NMR data for some of the new complexes

Complex	δ (ppm) ^a
Ru(η -CH ₃ C ₅ H ₄)Cl(PPh ₃) ₂	38.8s ^b
Ru(η -CH ₃ C ₅ H ₄)Cl(dppe)	79.7s ^b
Ru(η -CH ₃ C ₅ H ₄)Cl(tcep) ₂	24.3s ^c
Ru(η -CH ₃ C ₅ H ₄)(S ₂ OEt)(dppe)	79.85s ^b

^a Relative to external 85% H₃PO₄. ^b In chloroform. ^c In acetone.

(Table 3) indicate partial dissociation:



We have observed that the addition of HgCl₂ shifts the equilibrium to the right by the formation of the anion HgCl₃⁻ and the conductivity values correspond with those for a 1/1 electrolyte.

The higher conductivity of the dppe complex can be explained in terms of the better electron donor ability of the phosphine ligand, which in turn leads to more effective metal to nitrile donation of electron density [13]. The less basic tcep decreases the electron density on the metal and so strengthens the Ru-Cl bond, which remains unionized and unreactive [14].

Reactions with dithiolates

Complex II reacts with xanthates in methanol to give Ru(η -CH₃C₅H₄)(S₂-COR)(dppe) (R = Me (VII), Et (VIII)). These complexes show a strong band at ca. 1200 cm⁻¹ that can be attributed to a ν (C-O) of a monodentate xanthate (Table 1). The ³¹P NMR spectrum of complex VIII shows a singlet at 79.8 ppm that indicates the presence of two equivalent P atoms and supports the monodentate coordination of the xanthate group. As in the triphenylphosphine complexes [1], the presence of the xanthate ligand shifts the cyclopentadienyl proton resonances to lower field relative to those for the chloro complexes.

In contrast, similar reactions involving diethyldithiocarbamate lead to the replacement of both the chloride and cyclopentadienyl ligands and formation of Ru(S₂CNEt₂)₂(dppe) showing the high tendency of the dithiocarbamate and the bisphosphine to chelate the ruthenium atom; this contrasts with the monodentate behaviour of dithiocarbamate bonded to iron in the related Fp complex [10] (Fp = Fe(η -C₅H₅)(CO)₂).

Table 3

Conductivity data

Complex	Λ_M (ohm ⁻¹ cm ² mol ⁻¹) ^a	
	A	B
Ru(η -C ₅ H ₅)Cl(PPh ₃) ₂	10	65
Ru(η -C ₅ H ₅)Cl(dppe)	15.6	130
Ru(η -C ₅ H ₅)Cl(tcep) ₂	0.2	10

^a A: In 10⁻³ M acetonitrile solution. ^b B: After addition of one equivalent of HgCl₂.

The complexes containing tcep (IV–VI) do not react with dithiolates even upon prolonged reflux in methanol or acetone. This can be explained in terms of the lower lability of the Ru–Cl bond in these complexes.

The complex $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$, which shows no evidence of dissociation of the Ru–Cl bond [4], reacts with ethylxanthate in chloroform to give the monocarbonyl complex $\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{COEt})(\text{CO})$ (IX). In this compound the xanthate ligand acts as bidentate. The same reaction in refluxing acetone for 5 h gives a solid whose IR data show the presence of two carbonyl bands at 2020 and 1945 cm^{-1} and a $\nu(\text{CO})$ bond for a monodentate xanthate at 1150 cm^{-1} . This dicarbonyl is probably $\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{COEt})(\text{CO})_2$, but we could not obtain satisfactory analysis for it. The corresponding reaction between FpCl and $\text{NaS}_2\text{CNEt}_2$ in acetone solution also gives the known dicarbonyl $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNEt}_2)(\text{CO})_2$ [10].

Experimental

All reactions were carried out under oxygen-free nitrogen. $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ [15], $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CO}$) [1] and $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$ [16] were prepared by published methods. Analyses were by Elemental Microanalyses Ltd. (Devon). IR spectra were recorded on a Perkin–Elmer 1300 spectrophotometer with KBr pellets. ^1H and ^{31}P NMR spectra were recorded on a Varian EM-390 spectrometer at room temperature. Conductance measurements were performed with a Phillips Pr 9512100 conductivity cell.

Preparation of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{dppe})$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) (I–III)

A solution of 0.1 g (0.14 mmol) of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ and 0.055 g (0.14 mmol) of dppe in toluene (20 ml) was refluxed for 6 h. The volume was reduced to 5 ml and 20 ml of light petroleum were added. The faint yellow precipitate was filtered off, and the filtrate was kept cold overnight to give the product as orange crystals.

Preparation of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{tcep})_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) (IV–VI)

(a) A solution of 0.1 g (0.14 mmol) of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ and 0.06 g (0.3 mmol) of tcep in toluene (20 ml) was refluxed for 1.5 h. The greenish solid formed was filtered off and recrystallized by dissolution in acetone and reprecipitation as a yellow solid by addition of chloroform.

(b) A solution of 0.1 g of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{PPh}_3)_2$ and the equivalent amount of tcep in 20 ml of acetone was refluxed for 1 h. The solution was then concentrated to one third of its volume and cold chloroform was added. Yellow microcrystals of the product were obtained.

Reactions of $\text{Ru}(\eta\text{-CH}_3\text{C}_5\text{H}_4)\text{Cl}(\text{dppe})$

(a) *With xanthates.* An excess (0.2 mmol) of the potassium salt of methyl or ethylxanthate was added to a suspension of 0.1 g (0.16 mmol) of II in 30 ml of methanol. The mixture was refluxed for 2 h, then evaporated to dryness. Crystallization from dichloromethane/light petroleum gave yellow microcrystals of $\text{Ru}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{S}_2\text{COR})(\text{dppe})$ ($\text{R} = \text{Me}$, VII; $\text{R} = \text{Et}$, VIII).

(b) *With diethyldithiocarbamate.* A similar procedure to that described in (a) gave a yellow crystalline precipitate of $\text{Ru}(\text{S}_2\text{CNEt}_2)_2(\text{dppe})$ as the only product.

Preparation of Ru(η -C₅H₅)(S₂COEt)(CO) (IX)

A solution of 0.1 g (0.4 mmol) of Ru(η -C₅H₅)Cl(CO)₂ and 0.06 g of KS₂COEt in chloroform (15 ml) was refluxed for 2 h. Addition of light petroleum to this solution produced a brownish solid which was filtered off. Concentration of the filtrate and addition of more light petroleum gave complex IX as a yellow solid.

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References

- 1 L. Ballester Reventós and A. Gutiérrez Alonso, *J. Organomet. Chem.*, 309 (1986) 179.
- 2 G.S. Ashby, M.I. Bruce, I.B. Tomkins and R.C. Wallis, *Aust. J. Chem.*, 32 (1979) 1003.
- 3 T. Blackmore, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1971) 2376.
- 4 R.J. Haines and A.L. Du Preez, *J. Organomet. Chem.*, 84 (1975) 357.
- 5 G. Consiglio, F. Morandini and F. Bengertler, *Inorg. Chem.*, 21 (1982) 455; G. Consiglio, F. Morandini, G.F. Ciani and A. Sironi, *Organometallics*, 5 (1986) 1976.
- 6 A.N. Nesmeyanov, Y.A. Chapovsky and Y.A. Ustynyuk, *J. Organomet. Chem.*, 9 (1967) 345; R.D. Steward, J.J. Benedict, L. Isbrandt and R.S. Ampulski, *Inorg. Chem.*, 14 (1975) 2933 and ref. therein; G. Balavoine, M.L.H. Green and J.P. Savage, *J. Organomet. Chem.*, 128 (1977) 247.
- 7 R.J. Haines, A.L. Du Preez and I.L. Marais, *J. Organomet. Chem.*, 28 (1971) 405 and ref. therein.
- 8 D. Coucouvanis, *Progr. Inorg. Chem.*, 11 (1970) 311.
- 9 D. Catheline, E. Roman, D. Astruc, *Inorg. Chem.*, 23 (1984) 4508.
- 10 C. O'Connor, J.D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, (1969) 84.
- 11 E. Roman, D. Catheline and D. Astruc, *J. Organomet. Chem.*, 236 (1982) 229.
- 12 W.A. Henderson and C.A. Streuli, *J. Am. Chem. Soc.*, 82 (1960) 5791.
- 13 R. Adams, A. Davison and J.P. Selengue, *J. Am. Chem. Soc.*, 101 (1979) 7232.
- 14 N. Grie, S.C. Kao and R. Pettit, *J. Am. Chem. Soc.*, 101 (1979) 1627.
- 15 M.I. Bruce and N.J. Windsor, *Aust. J. Chem.*, 30 (1977) 1607.
- 16 T. Blackmore, J.D. Cotton, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 2931.