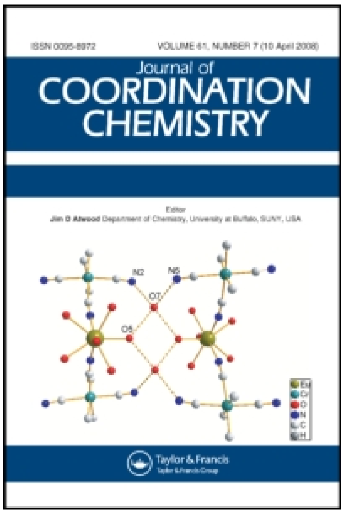

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REACTION OF Ru(η-RC_5H_4)Cl(PPh_3)$_2$ WITH CARBON DISULFIDE

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The reaction of carbon disulfide with Ru(η-C_5H_5)Cl(PPh_3)$_2$ gives [Ru(η-C_5H_5)(CS_2)(PPh_3)$_2$]$^+$ by two different routes. Photolysis of the starting chloro complex is also reported.

Keywords: Cyclopentadienyl, ruthenium, complexes, carbon disulfide

It is well known that the coordination chemistry of carbon disulfide affords several compounds that are excellent starting materials for organic and organometallic syntheses.[1] The use of carbon disulfide complexes is for example the most important method for the preparation of thiocarbonyl complexes.[2]

Among examples of carbon disulfide complexes of the platinum group metals, those of ruthenium are relatively rare;[3] even for cyclopentadienyl phosphine complexes, one of the most entensively studied classes for ruthenium, there is only one example involving an allene derivative, [Ru(η-C_5H_5)(CS_2)(PMe_3)$_2$]$^+$,[4] obtained by substitution of Ru(η-C_5H_5)Cl(PMe_3)$_2$. The facile substitution of the halogen as compared with Ru(η-C_5H_5)Cl(PPh_3)$_2$ is facilitated by the increased basicity of PMe_3.[5–8]

We now report the formation of new carbon disulfide derivatives from Ru(η-RC_5H_4)Cl(PPh_3)$_2$ (R = H, CH_3), obtained by chloride displacement.

RESULTS AND DISCUSSION

UV irradiation of a solution of Ru(η-C_5H_5)Cl(PPh_3)$_2$ in dichloromethane–carbon disulfide gives rise to a mixture of products, from which we have been able to isolate a green solid that analyzes for Ru(η-C_5H_5)Cl(CS_2)(PPh_3)$_2$ (**I**), and whose IR spectrum shows bands at 1000 and 1173 cm^{-1}, attributable to bonded CS_2. This solid is stable, but readily decomposes in solution to the starting material, thus precluding further studies on the coordination mode of carbon disulfide or complex stereochemistry.

As an alternative route, we have reacted [Ru(η-C_5H_5)(MeCN)(PPh_3)$_2$]$^+$ (obtained by refluxing[5] an acetonitrile solution of Ru(η-C_5H_5)Cl(PPh_3)$_2$ in the presence of $HgCl_2$ with CS_2 in dichloromethane during several days. The solid that precipitates was identified as [Ru(η-C_5H_5)(CS_2)(PPh_3)$_2$]($HgCl_3$), (**II**). The methyl analogue, [Ru(η-$CH_3C_5H_4$)(CS_2)(PPh_3)$_2$]BF_4 (**III**), has been obtained by the reaction of Ru(η-$CH_3C_5H_4$)Cl(PPh_3)$_2$ and $AgBF_4$ in the presence of an excess of carbon disulfide.

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TABLE I
Analytical and characteristic spectral data for the complexes.

	Analysis			IR (cm^{-1})		NMR (δ, ppm)		
	(calc	(found))	Λ_M					
Complex	C	H	($ohm^{-1}\,cm^2\,mol^{-1}$)	ν(C–S)	others	^1H	^{13}C	^{31}P
(I)	62.7	4.3		1000s				
	(62.9)	(4.4)		1170s				
(II)	47.0	3.2	108.3	860m	357m ν(Hg–Cl)	7.8–7.0m Ph	200.8s CS_2	41.8
	(47.0)	(3.3)		1275vs		4.46s Cp	133–128m Ph	
							80.2s Cp	
(III)	59.6	4.1	86.4	860m	1105br ν(BF_4)	7.4–6.8m Ph		
	(59.4)	(4.1)		1280vs		4.7m H2,5 Cp		
						3.1m H3,4 CP		
						2.1s CH_3		

Complexes (II) and (III) show IR bands at 860 and 1270–1280 cm^{-1} attributed to a dihapto carbon disulfide.[9] This coordination mode is supported by the NMR spectrum of (II). The ^{31}P NMR shows one singlet at 41.82 ppm for the two equivalent phosphine ligands, while the ^{13}C spectrum shows a signal at 200.8 ppm, characteristic of a π-bonded carbon disulfide. The cyclopentadienyl signal at 80.2 ppm is also observed.

The ^1H NMR spectrum of (II) shows a singlet at 4.46 ppm for the five cyclopentadienyl protons. This signal is split in the spectrum of (III), due to substitution in the ring; there are now two *pseudo* singlets at 4.72 ppm (for protons 2 and 5) and at 3.1 ppm (for protons 3 and 4). In both complexes the cyclopentadienyl signals appear shifted to lower field relative to the starting chloro complex, as is expected by the lowering of electronic density on the metal. A similar shift is also observed for the methyl resonance of the cyclopentadienyl group in (III). The cationic formulae of these complexes are supported by conductivity measurements that indicate that complexes (II) and (III) are 1:1 electrolites in solution. The carbon disulfide is weakly bonded in these complexes and is easily displaced by anionic ligands such as dithiolates, with the formation of $Ru(\eta\text{-}RC_5H_4)(S\text{–}S)(PPh_3)$.[8]

The results suggest that the formation of the CS_2 derivatives is related to the partial dissociation of the Ru–Cl bond, as observed in polar solvents,[6] and that this increases with the basicity of the phosphine attached to the metal. Thus, the complex $Ru(\eta\text{-}C_5H_5)Cl(P(CH_2CH_2CN)_3)_2$, with little dissociation due to the lower basicity of the phosphine,[10] does not react with CS_2 in polar solvents or in presence of $AgBF_4$, used to trap the chloride ligand.

EXPERIMENTAL

All reactions were carried out under oxygen-free nitrogen using dry solvents. $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ [11] and $Ru(\eta\text{-}CH_3C_5H_4)Cl(PPh_3)_2$ [8] were prepared using published methods. Analyses were by Elemental Microanalysis Ltd. (Devon). Spectrometers: IR, Perkin-Elmer 1300, samples in KBr discs; ^1H, ^{13}C and ^{31}P NMR, Bruker WP 80 SY at room temperature, TMS and 85% H_3PO_4 as standards. Conductivities were measured using a Philips PR9512100 conductivity cell in 10^{-3} M acetone solutions with excess CS_2. UV irradiation was performed with a 450 W Hanovia lamp.

Reaction of $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ *with* CS_2, (I)

A solution of $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ (0.73 g, 1 mmol) in 15 cm^3 dichloromethane–carbon disulfide (2:1), was irradiated for 2 h. The brownish solid that formed was filtered off and the solution concentrated *in vacuo* to 2 cm^3. Addition of cold hexane precipitated complex (I) as a green solid, which was washed with Et_2O and hexane. Yield: 0.41g (51%).

Preparation of $[Ru(\eta\text{-}C_5H_5)(CS_2)(PPh_3)_2](HgCl_3)$, (II)

A solution of 0.73 g (1 mmol) of $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ and 0.27 g (1 mmol) of $HgCl_2$ in 20 cm^3 acetonitrile was refluxed for five minutes, with a change in colour to yellow, due to the formation of $[Ru(\eta\text{-}C_5H_5)(MeCN)(PPh_3)_2]^+$.[5] This can be precipitated by addition of Et_2O. The complex thus obtained was dissolved in dichloromethane, 10 cm^3, and CS_2, 2 cm^3, was added. The solution was stirred for 3 days, with the appearance of a brown precipitate. Recrystallization of this solid from acetone/*n*-pentane afforded complex **(II)** as a yellow-orange solid. Yield: 0.65g (67% based on Ru(η-C_5H_5)Cl(PPh_3)$_2$).

Preparation of [Ru(η-$CH_3C_5H_4$)(CS_2)(PPh_3)$_2$]BF_4, (III)

A solution of 0.37 g (0.5 mmol) of Ru(η-$CH_3C_5H_4$)Cl(PPh_3)$_2$, 2 cm^3 of CS_2 and 0.1 g (0.6 mmol) of $AgBF_4$ in 10 cm^3 of acetone was refluxed for 5 minutes. The solvent was then removed *in vacuo* and the residue extracted with dichloromethane (2 × 5 cm^3). The filtrate was concentrated *in vacuo* to 3 cm^3. Addition of *n*-hexane to the orange solution afforded **(III)** as light orange microcrystals. Yield: 0.25 g (58%).

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