# **REACTIONS OF CARBONYL SULPHIDE AND CARBON DISULPHIDE WITH RUTHENIUM COMPLEXES**

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(Received 20 May 1988; accepted 6 July 1988)

Abstract—The reaction of COS with [Ru(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] under various experimental conditions resulted in the formation of chloro-bridged complexes  $[(Ph_3P)Cl(CO)Ru(\mu Cl_2Ru(CO)Cl(PPh_3)$  and  $[(PPh_3)_2Cl(CO)Ru(\mu-Cl)_2Ru(CO)Cl(PPh_3)_2]$  which reacted with excess PPh<sub>3</sub> under reflux to form  $[Ru(CO)Cl_2(PPh_3)_3]$ . CS<sub>2</sub> reacted with  $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$  in the presence of PPh<sub>3</sub> to give  $[(Ph_3P)_2Cl(CS)Ru(\mu-Cl)_2Ru(CS)]$  $Cl(PPh_3)_2$ ]. Reactions of COS with [RuH(CH<sub>3</sub>COO)(PPh<sub>3</sub>)<sub>3</sub>], [Ru(CO)Cl (CH<sub>3</sub>COO)(PPh<sub>3</sub>)<sub>2</sub>], [RuH(CO)Cl(AsPh<sub>3</sub>)<sub>3</sub>] and [Ru(CO)Cl<sub>2</sub>(AsPh<sub>3</sub>)<sub>3</sub>] resulted in the  $[Ru(CO)(CH_3COO)(PPh_3)_2]_2(\mu$ -S),  $\int [(Ph_3P)_2Cl(CO)]$ formation of the complexes 0

Ru-C-S-Ru(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>],  $\int [RuH(CO)_2Cl(AsPh_3)_2]$  and  $[Ru(CO)_2Cl_2(AsPh_3)_2]$ , [(Ph<sub>3</sub>As)<sub>2</sub>Cl(CO)Ru( $\mu$ -Cl)<sub>2</sub>Ru(CO)Cl(AsPh<sub>3</sub>)<sub>2</sub>], respectively. CS<sub>2</sub> reacted with [RuH(CH<sub>3</sub> COO)(PPh<sub>3</sub>)<sub>3</sub>] and [RuH(CO)Cl(AsPh<sub>3</sub>)<sub>3</sub>] to give [Ru(CS)(CH<sub>3</sub>COO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -S) and [RuH(CO)(CS)Cl(AsPh<sub>3</sub>)<sub>2</sub>], respectively. The complexes were characterized by elemental analysis, magnetic measurements, IR and electronic spectral studies.

The coordination properties of triatomics such as  $CO_2$ , COS and  $CS_2$ , which are the potential source of  $C_1$  chemistry, are interesting, especially from a synthetic view point. The interesting reactions, especially of  $CO_2$  and  $CS_2$ , are those which are related to (a) the formation of organometallic compounds, (b) the facile insertion into the M—H, M—C, M—N etc. bonds and (c) the catalytic synthesis of various types of organic compounds. <sup>1-20</sup> Since the first report of the reaction of COS, which is structurally similar to  $CO_2$  and  $CS_2$ , with a metal complex by Baird and Wilkinson, <sup>21</sup> it has received little attention. <sup>22</sup> Herein, we wish to report the reactions of COS and  $CS_2$  with ruthenium complexes.

### **EXPERIMENTAL**

All the reagents were of analytical or chemically pure grade. Benzene, toluene, hexane and diethyl ether were dried over sodium, dichloromethane over  $P_4O_{10}$  and methanol over CaO. All the solvents were purged with nitrogen and distilled immediately before use. All reactions were performed under pure dry nitrogen atmosphere.  $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$ ,  $[RuH(CH_3COO)(PPh_3)_3]$ ,  $[RuH(CO)ClL_3]$  (L = PPh<sub>3</sub>, AsPh<sub>3</sub>),  $[Ru(CO)Cl_2(AsPh_3)_3]$  and COS were prepared by literature methods.<sup>23-27</sup>

The analyses for sulphur and chloride in the complexes were carried out by the standard methods.<sup>28</sup> Carbon and hydrogen analyses were performed using a Carlo Erba 1106 Thomas CH Analyser 35. For the estimation of phosphorus and arsenic, samples were decomposed with sodium peroxide, sugar and sodium nitrate in the ratio 20:1:3 in a Parr bomb crucible and extracted with water. Then the solution was neutralized with dilute  $H_2SO_4$  and an excess of concentrated  $H_2SO_4$  (0.5 cm<sup>3</sup>) added. It was heated until the evolution of  $SO_3$  fumes ceased, then cooled and diluted with water. From the filtrate of the solution, phosphorus and arsenic were estimated by standard methods.<sup>29</sup> The results are reported in Table 1.

The IR spectra were recorded in the range 4000– $250 \text{ cm}^{-1}$  with a Perkin–Elmer 580 spectrophotometer from the R.S. Instrument Centre at the Indian Institute of Technology, Bombay. Samples were prepared as KBr pellets. Important IR frequencies are given in Table 2. The electronic

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Compounds	[Found (calc.)] (%)						
	С	Н	Cl	S	P/As		
$[Ru(CO)Cl(PPh_3)]_2(\mu-Cl)_2$	49.2	3.3	15.5		6.9		
	(49.3)	(3.2)	(15.3)		(6.7)		
$[Ru(CO)Cl(PPh_3)_2]_2(\mu-Cl)_2$	61.2	4.3	9.9		8.7		
	(61.3)	(4.1)	(9.8)		(8.5)		
$[Ru(CO)Cl_2(PPh_3)_3]$	66.8	4.7	7.3		9.6		
	(66.9)	(4.5)	(7.2)		(9.4)		
$[Ru(CS)Cl(PPh_3)_2]_2(\mu-Cl)_2$	59.8	4.2	9.7	4.4	8.5		
	(60.0)	(4.0)	(9.5)	(4.3)	(8.3)		
$[Ru(CO)(CH_3COO)(PPh_3)_2]_2(\mu-S)$	64.4	4.6		2.2	8.6		
	(64.3)	(4.5)		(2.1)	(8.5)		
$[Ru(CS)(CH_3COO)(PPh_3)_2]_2(\mu-S)$	62.8	4.6	—	6.5	8.5		
	(62.9)	(4.4)		(6.4)	(8.3)		
$[Ru(CO)Cl(PPh_3)_2]_2(\mu$ -COS)	62.5	4.3	5.0	2.2	8.7		
	(62.6)	(4.1)	(4.9)	(2.2)	(8.6)		
[RuH(CO) <sub>2</sub> Cl(AsPh <sub>3</sub> ) <sub>2</sub> ]	56.5	4.0	4.6		18.8		
	(56.6)	(3.8)	(4.4)		(18.6)		
[RuH(CO)(CS)Cl(AsPh <sub>3</sub> ) <sub>2</sub> ]	55.4	3.9	4.2	3.8	18.4		
	(55.5)	(3.7)	(4.3)	(3.9)	(18.2)		
$[Ru(CO)_2Cl_2(AsPh_3)_2]$	54.2	3.5	8.6		18.0		
	(54.3)	(3.6)	(8.4)		(17.8)		
$[Ru(CO)Cl(AsPh_3)_2]_2(\mu-Cl)_2$	54.8	3.6	8.8		18.6		
	(54.6)	(3.0)	(8.7)		(18.4)		

Table 1. Elemental analyses of the complexes

Table 2. Colour, melting point and important IR frequencies of the complexes

Compounds	Colour	М.р. (°С)	v(CO) (cm <sup>-1</sup> )	v(CS) (cm <sup>-1</sup> )	v(Ru—Cl) (cm <sup>-1</sup> )	v(Ru—S) (cm <sup>-1</sup> )
$[Ru(CO)Cl(PPh_3)]_2(\mu-Cl)_2$	Green	180	1950		330	
$(\mathbf{P}_{1})$ $(\mathbf{C}_{1})$ $(\mathbf{P}_{1})$ $(\mathbf{P}_{1})$ $(\mathbf{P}_{1})$	Orengo	760	1060		260	
$[Ru(CO)Ci(PPII_3)_2]_2(\mu-CI)_2$	Orange	208	1900	ALC: NOT	330 255	_
[Ru(CO)Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> ]	Orange	70	2025			
			1982			
			1945			
$[Ru(CS)Cl(PPh_3)_2]_2(\mu-Cl)_2$	Red	212		1290	335	
					265	
$[Ru(CO)(CH_3COO)(PPh_3)_2]_2(\mu-S)$	Green	150	1940		<u> </u>	460
$[Ru(CS)(CH_3COO)(PPh_3)_2]_2(\mu-S)$	Green	125		1290		460
$[Ru(CO)Cl(PPh_3)_2]_2(\mu$ -COS)	Yellow	230	1950			
[RuH(CO) <sub>2</sub> Cl(AsPh <sub>3</sub> ) <sub>2</sub> ]	White	280	2065		340	
			2005			
[RuH(CO)(CS)Cl(AsPh <sub>3</sub> ) <sub>2</sub> ]	Yellow	250	2030	1320	340	_
$[Ru(CO)_2Cl_2(AsPh_3)_2]$	Cream-white	140	2060			
			2000			
$[Ru(CO)Cl(AsPh_3)_2]_2(\mu-Cl)_2$	Red	160	1970		350	
					275	

spectra have been recorded with Shimadzu 160 spectrophotometer. Magnetic measurements were carried out by Gouy's method at room temperature  $(25^{\circ}C)$  using mercury tetrathiocyanato cobaltate(II) as calibrant. All the complexes were found to be dimagnetic. Melting points were determined by the capillary method and are uncorrected.

Synthesis of  $[(Ph_3P)Cl(CO)Ru(\mu-Cl)_2Ru(CO)Cl(PPh_3)]$  (1)

COS was bubbled into a solution of  $[\operatorname{Ru}(\operatorname{CH}_3\operatorname{CN})_2\operatorname{Cl}_2(\operatorname{PPh}_3)_2]$  (0.2 g) in toluene (30 cm<sup>3</sup>) for 30 min and the reaction mixture was stirred for 1 h. This was then evaporated to 5 cm<sup>3</sup> under reduced pressure. On the addition of *n*-hexane (40 cm<sup>3</sup>), a green complex (1) precipitated which was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield 0.08 g, 67%).

Synthesis of  $[(Ph_3P)_2Cl(CO)Ru(\mu-Cl)_2Ru-(CO)Cl(PPh_3)_2]$  (2)

COS was bubbled into a solution of  $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$  (0.2 g) and PPh<sub>3</sub> (0.4 g) in toluene (40 cm<sup>3</sup>) for 30 min and the reaction mixture was refluxed for 2 h. This was evaporated to 5 cm<sup>3</sup> and slow addition of *n*-hexane (40 cm<sup>3</sup>) precipitated a red complex (2) which was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield 0.065 g, 34%).

### Synthesis of [Ru(CO)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (3)

A solution of  $[(Ph_3P)Cl(CO)Ru(\mu-Cl)_2Ru$ (CO)Cl(PPh<sub>3</sub>)] (0.2 g) and PPh<sub>3</sub> (0.4 g) in benzene (30 cm<sup>3</sup>) was refluxed for 8 h whereby the colour of the solution changed from green to orange. The resulting orange solution was reduced in volume and *n*-hexane was added to give orange crystals of **3**.

Synthesis of  $[(Ph_3P)_2Cl(CS)Ru(\mu-Cl)_2Ru(CS)Cl(PPh_3)_2]$  (4)

A solution of  $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$  (0.2 g) and PPh<sub>3</sub> (0.6 g) in CS<sub>2</sub> (20 cm<sup>3</sup>) was refluxed for 3 h. The colour of the solution changed to red. The solution was diluted with diethyl ether (80 cm<sup>3</sup>) and cooled to 5°C. The red precipitate of 4 that formed was collected by filtration, washed with diethyl ether and dried *in vacuo* (yield 0.1 g, 52%).

### Synthesis of $[Ru(CO)(CH_3COO)(PPh_3)_2]_2(\mu-S)$ (5)

COS was bubbled into a solution of  $[RuH(CH_3 COO)(PPh_3)_3]$  (0.2 g) in toluene (20 cm<sup>3</sup>) for 30 min

and the reaction mixture was stirred for a further 1 h. Complex 5 was isolated by a similar procedure to that given for complex 1 (yield 0.12 g, 78%).

### Synthesis of $[Ru(CS)(CH_3COO)(PPh_3)_2]_2(\mu-S)$ (6)

A mixture of  $CS_2$  (2 cm<sup>3</sup>) and [RuH(CH<sub>3</sub>COO) (PPh<sub>3</sub>)<sub>3</sub>] (0.2 g) in toluene (20 cm<sup>3</sup>) was allowed to reflux for 1 h. The reaction mixture was evaporated to 5 cm<sup>3</sup> under reduced pressure. On addition of 40 cm<sup>3</sup> of *n*-hexane, complex **6** was precipitated which was centrifuged, washed with *n*hexane and dried *in vacuo* (yield 0.1 g, 64%).

## Synthesis of [Ru(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(µ-COS) (7)

COS was bubbled into a solution of  $[Ru(CO) Cl(CH_3COO)(PPh_3)_2]$  (0.2 g) in toluene (30 cm<sup>3</sup>) for 30 min and the reaction mixture was stirred for 1 h. Complex 7 was isolated by a similar procedure to that given for complex 1 (yield 0.13 g, 67%).

#### Synthesis of [RuH(CO)<sub>2</sub>Cl(AsPh<sub>3</sub>)<sub>2</sub>] (8)

COS was bubbled into a solution of  $[RuH(CO) Cl(AsPh_3)_3]$  (0.2 g) in toluene (30 cm<sup>3</sup>) for 30 min and the reaction mixture was stirred for 1 h. Complex 8 was isolated by a similar procedure to that given for complex 1 (yield 0.08 g, 54%).

### Synthesis of [RuH(CO)(CS)Cl(AsPh<sub>3</sub>)<sub>2</sub>] (9)

A solution of  $[RuH(CO)Cl(AsPh_3)_3]$  (0.2 g) in toluene (30 cm<sup>3</sup>) was treated with CS<sub>2</sub> (4 cm<sup>3</sup>) for 3 h. Complex 9 was isolated by a similar procedure to that given for complex 5 (yield 0.1 g, 65%).

### Reaction of COS with [Ru(CO)Cl<sub>2</sub>(AsPh<sub>3</sub>)<sub>3</sub>]

COS was bubbled into a solution of  $[Ru(CO) Cl_2(AsPh_3)_3]$  (0.2 g) in toluene (30 cm<sup>3</sup>) for 30 min. The reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was dissolved in a minimum of dichloromethane. On the addition of methanol, a cream white complex  $[Ru(CO)_2Cl_2(AsPh_3)_2]$  (10) separated, which was filtered, washed with methanol and diethyl ether and dried *in vacuo* (yield  $\approx 5\%$ ).

The filtrate was reduced to half the volume and cooled to 5°C. The red complex  $[(Ph_3As)_2 Cl(CO)Ru(\mu-Cl)_2Ru(CO)Cl(AsPh_3)_2]$  (11) which separated was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield 0.04 g, 43%).

#### **RESULTS AND DISCUSSION**

COS reacts with  $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$  at room temperature to give a green complex (1):

$$2Ru(CH_3CN)_2Cl_2(PPh_3)_2 + 2COS$$

$$\rightarrow [(Ph_3P)Cl(CO)Ru(\mu-Cl)_2Ru(CO)]$$

 $Cl(PPh_3)] + 2SPPh_3$ .

The reaction of COS with  $[Ru(CH_3CN)_2Cl_2 (PPh_3)_2]$  under reflux in the presence of PPh<sub>3</sub> yields an orange complex (2):

$$2Ru(CH_{3}CN)_{2}Cl_{2}(PPh_{3})_{2}+2COS$$

$$+2PPh_{3} \rightarrow [(Ph_{3}P)_{2}Cl(CO)Ru(\mu-Cl)_{2}$$

$$(CO)Cl(PPh_{3})_{2}]+2SPPh_{3}.$$

The green complex (1) or orange complex (2) reacts with excess PPh<sub>3</sub> under reflux to give orange complex  $[Ru(CO)Cl_2(PPh_3)_3]$  (3).

 $[Ru(CH_3CN)_2Cl_2(PPh_3)_2]$  in CS<sub>2</sub> under reflux in the presence of PPh<sub>3</sub> affords a red complex (4).

$$Ru(CH_{3}CN)_{2}Cl_{2}(PPh_{3})_{2}+2CS_{2}$$
$$+2PPh_{3} \rightarrow [(Ph_{3}P)_{2}Cl(CS)Ru(\mu-Cl)_{2}$$
$$(CS)Cl(PPh_{3})_{2}]+2SPPh_{3}$$

Reaction of  $[RuH(CH_3COO)(PPh_3)_3]$  with COS and CS<sub>2</sub> results in the formation of sulphur bridged carbonyl and thiocarbonyl complexes, respectively:

 $[RuH(CH_{3}COO)(PPh_{3})_{3}] + SCX$   $\rightarrow [Ru(CX)(CH_{3}COO)(PPh_{3})_{2}]_{2}(\mu-S) + \cdots$ (5), X = O; (6), X = S.

COS reacts with  $[Ru(CO)Cl(CH_3COO)(PPh_3)_2]$  to give the bridged carbonyl sulphide complex (7):

$$2Ru(CO)Cl(CH_3COO)(PPh_3)_2 + COS$$

$$\begin{array}{c} O \\ \parallel \\ \rightarrow (Ph_3P)_2Cl(CO)Ru - C - S - Ru(CO)Cl \\ (PPh_3)_2 + \cdots \end{array}$$

Reactions of SCX with [RuH(CO)Cl(AsPh<sub>3</sub>)<sub>3</sub>] give hydridodicarbonyl ruthenium complexes :

$$\rightarrow$$
 RuH(CO)(CX)CI(AsPn<sub>3</sub>)<sub>2</sub>+··

$$(8), X = O; (9), X = S$$

COS reacts with  $[Ru(CO)Cl_2(AsPh_3)_3]$  to give a cream-white complex,  $[Ru(CO)_2Cl_2(AsPh_3)_2]$  (10) and a red complex,  $[(Ph_3As)_2Cl(CO)Ru(\mu-Cl)_2Ru-(CO)Cl(AsPh_3)_2]$  (11).

#### IR spectra

Important IR data are summarized in Table 2. The IR spectrum of the green complex,  $[Ru(CO) Cl_2(PPh_3)]_2$ , shows absorption bands at 1950, 330 and 260 cm<sup>-1</sup> in addition to the characteristic bands of triphenylphosphine.<sup>30</sup> The band at 1950 cm<sup>-1</sup> is due to the characteristic stretching frequencies of the terminal carbonyl group. The band at 330 cm<sup>-1</sup> is typical of v(Ru—Cl) (Cl *trans* to Cl) while the band at 260 cm<sup>-1</sup> could be due to either v(Ru—Cl) (Cl *trans* to P) or to bridging chlorine modes, or to both.<sup>31</sup> The green complex (1) may, therefore, be dimeric in the solid state with bridging chlorines.



The IR spectrum of the orange complex [Ru(CO)  $Cl_2(PPh_3)_2$  shows absorption bands at 1960 cm<sup>-1</sup> due to v(CO), <sup>32</sup> 330 cm<sup>-1</sup> due to v(Ru—Cl) and 255  $cm^{-1}$  due to v(Ru-Cl) (bridging Ru-Cl modes). The IR spectrum of  $[Ru(CO)Cl_2(PPh_3)_3]$  contains carbonyl bands at 2025, 1982 and 1945 (same as the literature values)<sup>32</sup> indicating the presence of two isomers which could not be separated. One isomer of complex (3) has been reported previously with v(CO) at 1950 cm<sup>-1</sup>.<sup>33,34</sup> The IR spectrum of the thiocarbonyl complex  $[Ru(CS)Cl_2(PPh_3)_2]_2$ shows absorption bands at 1290 cm<sup>-1</sup> due to v(CS)(literature value 1290 cm<sup>-1</sup>),<sup>35</sup> and at 335 and  $265 \text{ cm}^{-1}$  due to v(Ru—Cl). The IR spectra of sulphide bridged complexes, [Ru(CX)(CH<sub>3</sub>COO)  $(PPh_3)_2]_2(\mu$ -S) (X = O, S), exhibit absorption bands at 1940 cm<sup>-1</sup> due to v(CO), at 1290 cm<sup>-1</sup> due to v(CS), at ca 460 cm<sup>-1</sup> due to v(Ru-S) and in the regions 1510, 1460  $\text{cm}^{-1}$  due to v(CO) of the acetate group, suggesting that the acetato ligand present is bidentate.<sup>36</sup> The IR spectrum of the carbonyl sulphide complex  $[(Ph_3P)_2Cl(CO)]$ 0

Ru—C—S—Ru(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>] contains a broad band at 1950 cm<sup>-1</sup> due to v(CO), a broad band at 1540 cm<sup>-1</sup> and a weak band at 850 cm<sup>-1</sup> due to the v(CO) and v(CS) of the COS group, respectively.<sup>37</sup> The IR spectrum of [RuH(CO)<sub>2</sub>Cl(AsPh<sub>3</sub>)<sub>2</sub>] shows absorption bands at 2065 and 2005 cm<sup>-1</sup> due to v(CO) (literature: 2060, 200 cm<sup>-1</sup>), the bands at 1985 cm<sup>-1</sup> may be due to v(Ru—H) and those at 340 cm<sup>-1</sup> are due to v(Ru—Cl). The IR spectrum of [RuH(CO)(CS)Cl(AsPh<sub>3</sub>)<sub>2</sub>] contains bands at 2030 cm<sup>-1</sup> due to v(CO), at 1320 cm<sup>-1</sup> due to v(CS), the one at 1985 cm<sup>-1</sup> may be due to v(Ru-H) and the one at 340 cm<sup>-1</sup> is due to v(Ru-Cl). The v(Ru-Cl)at 340 cm<sup>-1</sup> in these complexes indicates a chloride *trans* to carbonyl rather than to triphenylarsine. Therefore structures of complexes 8 and 9 tentatively may be given.



The structure for  $[RuH(CO)_2Cl(AsPh_3)_2]$  has been established by Harris and Robinson,<sup>26</sup> and for the analogous triphenylphosphine complex  $[RuH(CO)_2Cl(PPh_3)_2]$  by James and Markham.<sup>38</sup>  $[Ru(CO)Cl_2(AsPh_3)_2]$  contains strong bands at 2060 and 2000 cm<sup>-1</sup> due to v(CO) which are in the range reported previously for a *cis-trans-cis* type of isomer.<sup>33,39–41</sup> The IR spectrum of the complex, [di -  $\mu$  - chlorobis(chlorocarbonylbistriphenylarsine) ruthenium], exhibits absorption bands at 1970 cm<sup>-1</sup> (broad) due to v(CO) and at 350 and 275 cm<sup>-1</sup> due to v(Ru—Cl). One isomer of this complex has been previously reported with v(CO) at 1955 cm<sup>-1</sup>.<sup>26</sup>

#### Electronic spectra

The ground state of Ru<sup>II</sup> in an octahedral field  $(t_{2g}^6 \text{ configuration})$  is  ${}^1A_{1g}$ . The excited states corresponding to the  $t_{2g}^5e_g^1$  configuration are  ${}^3T_{1g}$ ,  ${}^3T_{2g}$ ,  ${}^1T_{1g}$  and  ${}^1T_{2g}$  in increasing order of energy. Thus one should expect four transitions,  ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ;  ${}^1A_{1g} \rightarrow {}^3T_{2g}$ ;  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ . In the electronic spectra of Ru<sup>II</sup> complexes, three bands in some cases, four or five bands in other cases, appear in the visible region (Fig. 1). The positions of these bands and their respective assignments are given in Table 3. From the band positions, the

	Band position		10 <i>Dq</i>	В	С		
Compounds	nm (ɛ)	(cm <sup>-1</sup> )	Assignments	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	β
$[Ru(CO)Cl(PPh_3)]_2(\mu-Cl)_2$	785(240) 520(508) 418(1606) 295(13636)	12738 19230 23923 33898	${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	22476	293	3246	0.47
[Ru(CO)Cl(PPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (µ-Cl) <sub>2</sub>	778(205) 527(477) 422(1205) 298(12525)	12853 18975 23696 33557	${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	22036	295	3061	0.47
$[Ru(CS)Cl(PPh_3)_2]_2(\mu-Cl)_2$	510(751) 410(956) 295(10327)	19607 24390 33898	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	22007	299	2400	0.48
[Ru(CO)(CH <sub>3</sub> COO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (μ-S)	558(271) 435(683) 297(14177)	17921 22988 33670	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	20321	316	2400	0.51
[Ru(CS)(CH <sub>3</sub> COO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (μ-S)	567(429) 432(709) 298(13776)	17636 23148 33557	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	20036	344	2400	0.55
[Ru(CO)Cl(PPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (µ-COS)	529(187) 428(706) 298(16125)	18903 23364 33557	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	21303	279	2400	0.45
RuH(CO) <sub>2</sub> Cl(AsPh <sub>3</sub> ) <sub>2</sub>	530(213) 420(592) 298(12232)	18867 23809 33557	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	21267	309	2400	0.49
RuH(CO)(CS)Cl(AsPh <sub>3</sub> ) <sub>2</sub>	536(144) 434(520) 300(10444)	18656 23041 33333	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	21056	274	2400	0.44
$[Ru(CO)Cl(AsPh_3)_2]_2(\mu-Cl)_2$	529(308) 435(756) 300(13761)	18903 22988 33333	${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ Charge-transfer	21303	255	2400	0.41



Fig. 1. Electronic absorption spectra of: (a)  $[Ru(CO) (CH_3COO)(PPh_3)_2]_2(\mu$ -S); (b)  $[Ru(CS)(CH_3COO) (PHh_3)_2]_2(\mu$ -S); (c)  $[Ru(CO)Cl(PPh_3)_2]_2(\mu$ -COS); (d)  $[Ru(CO)Cl(AsPh_3)_2]_2(\mu$ -Cl)\_2.

values of 10Dq, B,  $\beta$  and C have been calculated.<sup>42</sup> The values of the molar extinction coefficients for the bands in the range 400–500 nm were found to be more than those of the usual d-d transitions. This may be due to: (i) mixing of the energy levels with those corresponding to the neighbouring intense charge-transfer bands, (ii) the covalent nature of the complexes and (iii) the lowering of the symmetry to the molecule whereby the centre of symmetry is lost.

Acknowledgement—We thank the Council of Scientific and Industrial Research, New Delhi for financial assistance (Project No. 1(1026)/85-EMR-II).

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