# RUTHENIUM(II) COMPLEXES WITH MONO AND DITERTIARY ARSINES AND PHOSPHINES AND THEIR REACTION WITH SMALL MOLECULES

### M. M. TAQUI KHAN\*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

and

#### **RAFEEQ MOHIUDDIN**

Department of Chemistry, University College for Women, Hyderabad, India

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Abstract—Dichlorotetrakis(dimethylsulphoxide)ruthenium(II) reacts with AsPh<sub>3</sub>, AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph and SbPh<sub>3</sub> in ethanolic hydrochloric acid solution to yield the complexes RuCl<sub>2</sub>(DMSO)<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>, RuCl<sub>2</sub>(DMSO) L<sub>2</sub> (L = AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph, SbPh<sub>3</sub>) respectively. The treatment of ruthenium(II) blue solution with AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph and SbPh<sub>3</sub> in alcohol resulted in the formation of the complexes; RuCl<sub>2</sub>L<sub>3</sub> (L = AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph and SbPh<sub>3</sub>), respectively.

The reaction of  $RuCl_2(DMSO)_4$  with the bidentate ligands 1,2 bis (diphenylarsino)methane (DPAM), 1,2 bis(diphenylarsino)ethane (DPAE) and 1,2 bis (diphenylphosphino)methane (DPPM). 1,2 bis(diphenylphosphino)ethane (DPPE), in ethanol gave the complexes  $RuCl_2(DPAM)_2$ ,  $RuCl_2(DPAE)_2$ ,  $RuCl_2(DPPM)_2$   $RuCl_2(DPPE)_2$ , respectively. The complexes thus obtained undergo reaction with carbon monoxide, hydrogen, molecular nitrogen and nitric oxide to yield a variety of mixed ligand complexes.

During the last decade extensive research has been carried out on ruthenium(II) complexes of tertiary phosphines especially Wilkinsons's complex RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>.<sup>1,2</sup> In contrast to the tertiary phosphine complexes, there are very few reports on ruthenium(II) complexes with monotertiary arsines. Some of these complexes include  $RuCl_{2}(AsMePh_{2})_{4}^{3}$  and  $RuCl_{2}(AsMe_{2}Ph)_{4}^{4}$  that were obtained by the interaction of RuCl<sub>3</sub> with AsMePh<sub>2</sub> or AsMe<sub>2</sub>Ph, respectively. However, RuCl<sub>3</sub> is not a very good source of ruthenium(II) since reduction to the ruthenium(II) state by the less basic arsine ligands in high boiling solvents invariably results in the formation of either polymers or chlorobridged dimers.<sup>5</sup> Thus, reaction of  $RuCl_3$  with ethyldiphenylarsine in the presence of acid yielded  $Ru_2Cl_3(AsEtPh_2)_6Cl$  with triple chloro bridges.<sup>6</sup>

A number of ruthenium(II) complexes were reported with bidentate ligands. Thus interaction of ruthenium(III) halide with o-phenylene-bisdimethylarsine(diars) produces  $RuX_2(diars)_2^7$ . Similar preparative method with the ditertiary phosphines, diphos, (1,2 bis(diphenylphosphino)ethane, 1,2 bis(diphenylphosphine)methane and o-phenylenebis(dimethylphosphine) gave  $RuCl_2(diphos)_2$ .<sup>8</sup> The diarsine complexes prepared by this method include *trans*-RuCl\_2(DPAE)\_2 and *trans*-RuCl\_2(DPAM)\_2 (DPAE = 1,2 bis(diphenylarsino) ethane, DPAM = 1,2 bis(diphenylarsino) methane).<sup>9</sup>

In the present work attempts were made to prepare monomeric ruthenium(II) complexes with a variety of monodentate arsines and bidentate

<sup>\*</sup>Present address: Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, Gujarat, India.

phosphines and arsines. The complex  $RuCl_2$  (DMSO)<sub>4</sub><sup>10,11</sup> was employed as a suitable starting material for the synthesis of Ru(II) complexes with mono and bidentate phosphines and arsines. The blue solution<sup>12</sup> prepared by the reduction of RuCl<sub>3</sub> with zinc amalgam was also employed successfully for the synthesis of Ru(II) complexes with monodentate ligands. The Ru(II) complexes thus obtained activate small molecules like H<sub>2</sub>, N<sub>2</sub>, CO and NO to yield a variety of mixed ligand complexes of mono or bidentate ligands with the small molecules.

#### **EXPERIMENTAL**

The ligands, triphenylstibine, 1,2-bis(diphenylphosphino)methane (DPPM),1,2-bis(diphenylarsino)methane (DPAM),1,2-bis(diphenylphosphino)ethane (DPPE),1,2-bis(diphenylarsino) ethane (DPAE) were obtained from Ventron Corp., U.S.A. Triphenylarsine was from Maybridge Chemical Co., U.K. The arsine ligands, methyldiphenylarsine and dimethylphenylarsine were prepared by reacting the respective methyliodoarsines with methylmagnesium bromide in dry ether. Methyliodoarsine and dimethyliodoarsine were prepared by standard methods.<sup>13</sup> The reaction products were purified by vacuum distillation. Hydrated ruthenium trichloride (RuCl<sub>3</sub>·3H<sub>2</sub>O) was purchased from Alfa Ventron, U.S.A. and also from Johnson Matthey (England). The complexes RuCl<sub>2</sub>(DMSO)<sub>4</sub><sup>10,11</sup> and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>1,2</sup> were synthesized by published procedures. All organic solvents and acids used were BDH Analar grade.

The gases used in this work, carbon monoxide and nitric oxide were prepared and purified by standard procedures. Pure molecular hydrogen was obtained by electrolysis of a 20% solution of sodium hydroxide in a U-tube fitted with nickel electrodes and the gas dried by passing through a calcium chloride tower. Nitrogen gas obtained commercially was freed from oxygen and moisture by passing through vanadium(II) sulphate and alkaline pyrogallol solutions and finally through ascarite. Vanadium(II) sulphate solution was prepared by reduction of vanadyl(IV) sulphate solution by passing the solution through a column filled with zinc amalgam. All the complexes reported in this work were prepared under purified nitrogen atmosphere using the Schlenk tube technique.

The elemental analysis of the elements carbon, hydrogen and chlorine was performed by the Microanalytical service, CSIRO Australia and Chemalytics Inc., Tempe, Arizona, U.S.A., IR spectra were recorded on a Beckman IR-12 spectrophotometer. The NMR spectra were recorded on Varian A-60 and HA-100 spectrometers. The electronic spectra were measured in methanolchloroform or dichloromethane solvents using Cary Model-14 and Carl Zeise DMR-2 spectrometers. Conductance data were obtained in dimethylacetamide (DMA) solution using a systronic conductance bridge and a cell which had been calibrated with 0.1 M aqueous potassium chloride solution.

#### PREPARATIONS

#### (1) Dichlorobis(dimethylsulphoxide)bis(triphenylarsine)ruthenium(II)

A solution of 0.24 g (0.5 mmol)of RuCl<sub>2</sub>(DMSO)<sub>4</sub> in 10 cm<sup>3</sup> of ethanol and 3 cm<sup>3</sup> of concentrated hydrochloric acid was refluxed for about 15 min. To the hot solution was added an ethanolic solution of triphenylarsine (0.612 g, 2 mmol) and refluxed for about 6 hr. The colour of the solution changed from orange to brown. The solution was evaporated to a small volume under reduced pressure and the orange brown complex was precipitated by dissolving in acetone and reprecipitating with ether. The same complex was also prepared by heating 0.24 g of RuCl<sub>2</sub>(DMSO)<sub>4</sub> and excess of triphenyl arsine (1.530 g, 5 mmol) dissolved in a mixture of ethanol and hydrochloric acid (70 and 7 cm<sup>3</sup> respectively) in a sealed tube at 70°C for about 48 hr. At the end of the reaction period a green complex separated which was filtered and washed with methanol. The complex was recrystallised from dichloromethane and acetone.

# (2) Dichloro(dimethylsulphoxide)tris(diphenylmethylarsine)ruthenium(II)

About 0.24 g (0.5 mmol) of RuCl<sub>2</sub>(DMSO)<sub>4</sub> was dissolved in 10 cm<sup>3</sup> of ethanol and 3 cm<sup>3</sup> of concentrated hydrochloric acid was added and the solution refluxed for about 15 min. To the hot solution was added methyldiphenylarsine (0.9 gm, 3 mmol) in 20 cm<sup>3</sup> of ethanol and refluxed for about 6 hr. The colour of the solution was evaporated to a small volume and the chocolate brown complex was precipitated by the addition of petroleum ether and recrystallised from dichloromethane and ether.

# (3) Dichloro(dimethylsulphoxide)tris(dimethylphenylarsine)ruthenium(II)

A solution of 0.24 g (0.5 mmol) of RuCl<sub>2</sub> (DMSO)<sub>4</sub> in 10 cm<sup>3</sup> of ethanol and 3 cm<sup>3</sup> of concentrated hydrochloric acid was refluxed for about 15 min. To the hot solution was added a solution of dimethylphenylarsine (0.846 g, 3 mmol) and refluxed for about 6 hr. The solution was evaporated to a small volume and cooled to  $-25^{\circ}$ C by keeping in dry ice. The orange complex was precipitated by the addition of petroleum ether (40-60 grade). The complex was recrystallised from dichloromethane and ether.

#### (4) Dichloro (dimethylsulphoxide) tris (triphenylstibine) ruthenium (II)

A mixture of  $RuCl_2(DMSO)_4$  (0.24 g, 0.5 g, 0.5 mmol) and triphenylstibine (0.704 g, 2 mmol) in 30 cm<sup>3</sup> of ethanol was refluxed for about 3 hr. The solution turned yellowish orange from brown. The pink powder separated was filtered and washed with methanol. The complex was recrystallised either from alcohol or dichloromethane.

#### (5) Dichlorotris(methyldiphenylarsine)ruthenium-(II)

## (6) Dichlorotris(dimethylphenylarsine)ruthenium-(II)

These complexes were prepared by the addition of 6 mmol of methyldiphenyl or dimethylphenylarsine to an alcoholic blue solution obtained by refluxing ruthenium trichloride (0.208 g, 1 mmol) with zinc amalgam for 30 min. Zinc was removed from the solution and 3–4 cm<sup>3</sup> of hydrochloric acid added. The mixture was further refluxed in the presence of the appropriate ligand for 3–4 hr. For the methyldiphenylarsine complex, solvent was removed under vacuum and the brown complex precipitated by the addition of acetone and recrystallised from dichloromethane and ether. The dimethylphenyl arsine complex separated as yellow crystals was filtered, washed with acetone and methanol and recrystallised from alcohol.

## (7) Dichlorotris(triphenylstibine)ruthenium(II)

Ruthenium trichloride (0.208 g, 1 mmol) was refluxed with zinc amalgam in alcohol for about 30 min. Zinc was removed and to the blue solution triphenylstibine (1.408 g, 4 mmol) in alcohol was added. The solution was refluxed for about  $2\frac{1}{2}$  hr. A pink coloured solid separated which was filtered and washed with methanol. The complex was recrystallised from alcohol.

## (8) Dichlorobis {1,2-bis (diphenylarsino)methane } ruthenium(II)

# (9) Dichlorobis {1,2-bis(diphenylphosphino)methane }ruthenium(II)

To a solution of  $RuCl_2(DMSO)_4$  (0.242 g, 0.5 mmol) in 10 cm<sup>3</sup> of ethanol, was added a solution of the appropriate ligand (1 mmol) in 30 cm<sup>3</sup> of ethanol. The mixture was refluxed for about 4 hr. Lemon yellow crystals in the case of  $RuCl_2(DPPM)_2$  and orange crystals in case of  $RuCl_2(DPAM)_2$  were filtered, washed with methanol and ether. The complexes were recrystallised from dichloromethane.

# (10) Dichlorobis {1,2-bis(diphenylphosphino)ethane {ruthenium(II)

This complex was prepared by a method simpler than that of Chatt and Hayter.<sup>8</sup> 1,2 bis (diphenylphosphino)ethane (0.796 g, 2 mmol) in 20 cm<sup>3</sup> of ethanol was added to a solution of RuCl<sub>2</sub>(DMSO)<sub>4</sub> (0.242 g, 0.5 mmol) in 15 cm<sup>3</sup> of ethanol and the solution refluxed for about 2 hr. The colour changed from dark orange to bright lemon-yellow. The lemon-yellow crystals separated were filtered and washed with methanol. The complex was recrystallised from dichloromethane.

#### (11) Dichlorobis {1,2-bis (diphenylarsino) ethane }ruthenium (II)

This complex was earlier reported by Mague and Mitchener.<sup>9</sup> The complex was synthesized by a method simpler than earlier reported whereby the refluxing time was reduced and a good yield was obtained. The complex  $RuCl_2(DMSO)_4$ , (0.484 g, 1 mmol) was dissolved in 10 cm<sup>3</sup> of ethanol and 1,2 bis(diphenylarsino)ethane (0.480 g, 1 mmol) in 30 cm<sup>3</sup> of ethanol were refluxed for about 2 hr. Orange yellow crystals separated, which were filtered and washed with methanol. The complex was recrystallised from dichloromethane.

(12) Dichloro-dicarbonyl(dimethylsulphoxide)(triphenylarsine)ruthenium(II).

(13) Dichloro-dicarbonyl-bis(methyldiphenylarsine)ruthenium(II).

(14) Dichloro-dicarbonyl-bis(dimethylphenylarsine)ruthenium(II).

(15) Dichloro-dicarbonyl-bis(triphenylstibine)ruthenium(II).

(16) Dichloro-carbonyl-tris(triphenylstibine)ruthenium(II).

(17) Dichloro-dicarbonyl-bis {1,2-bis(diphenylarsino)methane }ruthenium(II).

(18) Dichloro-dicarbonyl-bis {1,2-bis(diphenylphosphino)methane }ruthenium(II) (19) Chloro-carbonyl-bis {1,2-bis (diphenylphos-Phino)ethane }ruthenium (II)chloride.
(20) Chloro-carbonyl-bis {1,2-bis (diphenylarsino)ethane }ruthenium (II).

In a general method of preparation of the carbonyls, about 0.02 mmol of the complex (1-4), (8-11) was dissolved in dry chloroform and a stream of carbon monoxide was passed through the solution until there was no further colour change. The solutions were concentrated to a small volume and the carbonyls (12-20) precipitated by the addition of petroleum ether, filtered and dried.

(21) Hydrido-chloro-bis(dimethylsulphoxide)bis-(triphenylarsine)ruthenium(II).

(22) Hydrido-chloro-(dimethylsulphoxide)tris(methyldiphenylarsine)ruthenium(II).

(23) Hydrido-chloro-(dimethylsulphoxide)tris(dimethylphenylarsine)ruthenium(II).

(24) Hydrido-chloro-tris(methyldiphenylarsine)ruthenium(II).

Molecular hydrogen was bubbled through a 0.02 m molar dimethylformamide solution of complexes (1)/(3), (5), for about 12 hr at 40°C. The dark brown hydrides were isolated by removing the solvent under vacuum and precipitation by petroleum ether.

(25) Hydrido (dinitrogen)bis (dimethylsulphoxide)bis (triphenylarsine)ruthenium (II)chloride
(26) Hydrido (dinitrogen)dimethylsulphoxide-tris-(methyldiphenylarsine)ruthenium (II)chloride.

Molecular hydrogen was passed through a 0.02 m molar dimethylformamide solution of the complexes (1) and (2) and molecular nitrogen bubbled through the solution for about 24 hr. The mixed ligand hydrido-dinitrogen complexes were isoalted by removing the solvent under vacuum and addition of petroleum ether.

(27) Dichloro-nitrosyl-(dimethylsulphoxide)bis(triphenylarsine)ruthenium(II).

(28) Dichloro-nitrosyl-(dimethylsulphoxide)bis(methyldiphenylarsine)ruthenium(II).

(29) Dichloro-nitrosyl-(dimethylsulphoxide)bis(dimethylphenylarsine)ruthenium(II).

(30) Dichloro-nitrosyl-(dimethylsulphoxide)bis(triphenylstibene)ruthenium(II).

(31) Dichloro-nitrosyl-tris(methyldiphenylarsine)ruthenium(II).

(32) Dichloro-nitrosyl-bis(diphenylphosphinomethane)ruthenium(II). (33) Dichloro-nitrosyl-bis(diphenylarsinoethane)ruthenium(II).

Nitric oxide was passed through a 0.02 mmol chloroform solution of complexes (1-5), (9) and (11) for about 24 hr until there was no further colour change. The solutions were concentrated to a small volume and the nitrosyls precipitated by the addition of petroleum ether.

#### **RESULTS AND DISCUSSION**

Tables 1 and 2 present the analytical data and the molar conductivities of the ruthenium(II) complexes with mono and bidentate tertiary arsines and phosphines. IR spectra of these complexes are given in Table 3. The NMR and electronic spectra of some of the complexes are given in Tables 4 and 5 respectively.

A brown complex (1) was obtained by the displacement of two molecules of coordinated DMSO by AsPh<sub>3</sub> from RuCl<sub>2</sub>(DMSO)<sub>4</sub>. X-Ray structure of the parent complex RuCl<sub>2</sub>(DMSO)<sub>4</sub> had indicated two different types of coordination of DMSO groups; three DMSO groups are bonded through sulphur and one through oxygen to the metal ion<sup>14</sup> with *cis*-chlorides. When RuCl<sub>2</sub> (DMSO)<sub>4</sub> reacts with triphenylarsine the weakly O-bonded DMSO group gets displaced first followed by one of the S-bonded DMSO groups to give the complex RuCl<sub>2</sub>(DMSO)<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub> with cischlorides. The vM-Cl is expected to give two bands. Although a sharp peak is obtained at  $320 \text{ cm}^{-1}$  the other band must have been masked by the DMSO peak. The band at 1075 cm<sup>-1</sup> indicative of S-bonded DMSO was observed but no band appeared around 900 cm<sup>-1</sup> which could be attributed to O-bonded DMSO.15 The metal-arsine and metal-sulphur absorptions overlap in the complex and the peak at  $480 \text{ cm}^{-1}$  could not be assigned unequivocally to any of these vibrations. The complex is assigned a  $C_h$  geometry as shown in Fig. 1.

A green modification of complex (1) was obtained when  $RuCl_2(DMSO)_4$  and triphenylarsine were refluxed in a sealed tube. The preparation in the sealed tube was attempted with an idea to completely displace dimethylsulphoxide by triphenylarsine in  $RuCl_2(DMSO)_4$  complex. The green complex shows an IR spectrum identical to that of the brown complex.

Two geometrical isomers are possible for the complex  $\text{RuCl}_2(\text{DMSO})_2(\text{AsPh}_3)_2$ , one with *cis* dispositions of DMSO, triphenylarsine and *cis* chlorides (Fig. 1) and the other with *cis* dispositions of DMSO, the chloride and *trans* disposition of triphenylarsine (Fig. 2).

S.No	. Complex	Colour	с	Analysis <sup>+</sup> H	(\$) Cl	м.р. °С	Molar Gondugtance in DMA. (Ohms ., Cm , equi )
1.	RuCl <sub>2</sub> (DMSO) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>	Orange brown	51.13 (51.13)	4.20 (4.40)	8.60 (7.60)	106*	25.12
2.	$\operatorname{RuCl}_2(\operatorname{DMSO})(\operatorname{AsMePh}_2)_3$	Chocolate brown	49.70 (50.10)	4.30 (4.50)	9.80 (7.30)	118*	16.62
3.	RuC12(DMSO)(AsMe2Ph)3	<u>Yellowish</u> green	38.05 (39.19)	4.75 (4.90)	9.20 (8.92)	130*	23.86
<b>b</b> .	RuCl <sub>2</sub> (DMSO)(SbPh <sub>3</sub> ) <sub>3</sub>	Pink	51.40 (51.33)	3 <b>.94</b> (3 <b>.</b> 90)	4.80 (5.40)	239	11.25
5.	RuCl <sub>2</sub> (AsMePh <sub>2</sub> ) <sub>3</sub>	Brown	46.76 (48.78)	4.49 (4.31)	6.90 (7.85)	165*	14 .90
6. M	RuCl <sub>2</sub> (AsMe <sub>2</sub> Ph) <sub>3</sub>	Yellow	41.65 (40.11)	4.87 (4.60)	8.88 (9.88)	191*	31.78
<b>?∙</b>	RuCl <sub>2</sub> (SbPb <sub>3</sub> ) <sub>3</sub>	Pink	53.40 ( <b>9</b> 2.64)	3.83 (3.65)	5.50 (5.76)	2 <b>50</b> *	37.70
8. ~	RuCl <sub>2</sub> (DPAM)	Orange	53.78 (52.68)	3.86 (3.76)	5.40 (6.36)	215	30•38
2.	RuCl <sub>2</sub> (DPPM) <sub>2</sub>	Lemon Yellow	59.67 (62.50)	4.38 (Կ.ԿՇ)	5.86 (6.97)	260*	32 •50
10.	RuCl <sub>2</sub> (DPPE) <sub>2</sub>	Yellow	64.08 (64.08)	4.09 (4.97)	6.54 (7.33)	260*	12.00
11.	RuCl <sub>2</sub> (DPAE)2	Orange	54.42 (54.64)	4.34 ) (4.20)	5.50 (6.21)	255*	20.41

Table 1. Analytical data for ruthenium(II) complexes

#### \* decomposed

(+ calculated values in paranthesis)



Fig. 1.



The brown isomer will have a  $C_h$  symmetry while the green isomer will have a  $C_{2\nu}$  symmetry. The two isomers cannot be distinguished on the basis of IR spectra which indicate cis-chlorides in both the complexes. Dipole moment measurements gave almost identical values within experimental error of 1.18 Debye for the brown and 1.3 Debye for the green isomers, respectively. This is expected because both the compounds have cis-chlorides, and a cis or trans disposition of other less polar groups cannot make a significant difference in dipole moments. However, these two isomers were characterized on the basis of their NMR spectra. The NMR spectrum of the brown complex with non-equivalent sets of ligands exhibited two multiplets of equal intensity at  $2.15\tau$  and  $2.65\tau$  which may be assigned to the phenyl protons of cistriphenylarsines. The methyl protons of cis-DMSO groups also appeared as two multiplets at 6.657 and 7.757. The NMR spectrum of the brown compound thus supports a  $C_h$  symmetry for the complex.

In the NMR spectrum of the green isomer of (1) the phenyl protons of triphenylarsine exhibit a

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Table 2. Analytical data for ruthenium(II) complexes

		_		ANA	LYSIS (%)		
S.No.	Complex	Colour	C	н	C1	0	N
12.	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{DMSO})(\operatorname{AsFh}_3)_2$	Yellow	43.03 (43.13)	2.40 (2.45)	11.00 (11.60)	7.20 (7.84)	-
<u>13</u> .	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{AsMePh}_2)_2$	Yellow	52.03 (52.41)	4.00 (4.05)	11.00 (11.07)	4.55 (4.99)	-
14.	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{AsMe}_2\operatorname{Ph})_2$	Yellow	36.02 (36.48)	3.05 (3.71)	11.03 (11.99)	5.02 (5.40)	-
15.	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{SbPh}_3)_2$	Orange	52.30 (53.20)	3.50 (3.69)	8.00 (8.74)	3.50 (⊴.94)	-
16.	BuCl <sub>2</sub> (CO)(Sbrh <sub>3</sub> ) <sub>3</sub>	Orange	56.00 (56.63)	3.40 (3.82)	9.00 (9.06)	2.00 (2.04)	-
17.	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{DPAW})_2$	Yallow	53.0) (53.24)	3.45 (3.75)	5.35 (6.05)	2.45 (2.73)	-
13.	$\operatorname{RuCl}_2(\operatorname{CO})_2(\operatorname{Dr}\operatorname{FM})_2$	Yallow	62.25 (62.65	4.05 (4.45)	6.30 (7.13)	3.00 (3.21)	-
19. M	$\left[\operatorname{RuC1}(\operatorname{CO})(\operatorname{DPPE})_2\right]C_1$	Yallow	63.25 (63.85)	4.60 (4.32)	7.00 (7.12)	1.40 (1.60)	-
20.	Ruci(CO)(JPAE)2]C1	Yellow	54.08 (54.26)	4.00 (4.09)	6,00 (6,05)	1.26 (1.36)	-
21 <b>.</b>	RuHC1(JMG0) <sub>2</sub> (Asrh <sub>3</sub> ) <sub>2</sub>	Dark brown	52,89 (53,00)	4.80 (4.74)	3.31 (3.92)	ತಿ,42 (೧,53)	
22.	RuнC1(DaSO)(AsMe <sub>2</sub> Ph) <sub>3</sub>	Dark brown	51.82 (51.93)	5,00 (4,35)	3.80 (3.74)	1.70 (1.63)	-
23 <b>.</b>	RubC1(Jd30)(AsMe2Fh)3	Jark Drown	41.00 (40.93)	5.00 (5.25)	4.30 (4.56)	1.99 (2.10)	-
24 <b>.</b>	$RuHCl(AsMert2)_{3}$	Dark brown	51.00 (50.71)	4,35 (4.60)	4,00 (4,03)	-	-
25.	$\left[ \frac{\text{RuHN}_2(\text{uMSC})_2(\text{Asth}_3)_2}{2} \right] C1$	Brown	51.30 (51.42)	4.30 (4.60)	3 <b>.60</b> (3.90)	3.50 (3.42)	2 87 (2 <b>.</b> 99)
<u>26</u> .		Brown	50.30 (50.43)	4,61 (4,71)	3.50 (3.64)	1.70 (1.64)	2.75 (2.87)
27.	$\operatorname{RuCl}_2(\mathbb{N}0)(\operatorname{UMSO})(\operatorname{AsPh}_3)_2$	Chocclate brown	51.20 (51.12)	4.00 (4.03)	7.35 (7.95)	2.68 (3.58)	1,47 (1,57)
<u>28</u> .	$RuCl_2 NO(DMSO)(AsMePh_2)_2$	Brown	43.60 (43.75)	4.00 (4.16)	9.03 (9.24)	4.05 (4.16)	1.73 (1.32)
29.	$\operatorname{RuCl}_{2}(\operatorname{NO})(\operatorname{DMSO})(\operatorname{AsMe}_{2}\operatorname{Ph})_{2}$	Brown	34.00 (33.54)	4.21 (4.34)	11.07 (11.02)	5.01 (4.96)	2.04 (2.17)
<u>30</u> .	$\operatorname{RuCl}_2(\operatorname{NO})(\operatorname{DMSO})(\operatorname{SbPh}_3)_2$	Buff	46.03 (46.34)	3.70 (3.65)	7.05 (7.21)	3.05 (3.25)	1.44 (1.42)
31.	$\operatorname{RuCl}_2(\operatorname{NO})(\operatorname{AsMe}^{\operatorname{Ph}}_2)_3$	Chocolate brown	50.00 (49.60)	4.50 (4.38)	8.00 (7.98)	1.82 (1.79)	1.60 (1.57)
32.	Ruc1 <sub>2</sub> (NC)(DFrM) <sub>2</sub>	Brown	51.69 (61.85)	4.75 (4.53)	7.43 (7.32)	1.72 (1.65)	1.47 (1.44)
33.	$\operatorname{RuCl}_2(NO)(\operatorname{DPAd})_2$	Brown	53.05 (53.15)	4.10 (4.08)	6.08 (6.04)	1.38 (1.36)	1.21 (1.19)

(+) Calculated values in parenthesis.

single multiplet at  $3.6\tau$  and methyl protons of DMSO a multiplet at  $8.8\tau$ . This is in accord with a *trans*-deposition of the triphenylarsine and *cis* disposition of DMSO and chloride groups in the compound with a point group  $C_{2\nu}$ .

The electronic spectrum of the brown isomer of

(1) gives charge transfer bands characteristic of the presence of both DMSO<sup>16</sup> and triphenylarsine<sup>17a,b</sup> in the coordination sphere of the metal ion. The electronic spectrum of DMSO gives absorption bands at 200 and 210 nm that can be assigned to the  $\sigma - \sigma^*$  and  $n - \pi^*$  transitions of the ligand,

Ruthenium(II) complexes with mono and ditertiary arsines and phosphines

S.No.	Complex	<b>V</b> (M-Cl)cm <sup>-1</sup>	)/(M-DMS0)cm <sup>-1</sup>	b (M-L)cm <sup>-1</sup> (L=P or As	) Other bands cm <sup>-1</sup>
1.	RuCl <sub>2</sub> (DHSO) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>	320(s)	480(s),1025(m) 1075(m),1430(s)	480(s)	660(m)690(s),735(s),1000(m), 1485(m)
2.	RuCl <sub>2</sub> ( 1KSO)(AsMePh <sub>2</sub> ) <sub>2</sub>	324(s)	480(s),1025(s), 1075(s),1435(s)	480(s)	660(m)690(m),735(s),800(s), 1000(m), 1485(m)
¥.	RuCl <sub>2</sub> (DMSO)(Ashe2Ph33	330(s)	485(s),1065(s), 1430(s)	485(s)	670(w),695(m),730(s),800(s), 990(m)
¥.	RuCl <sub>2</sub> (DMSO)(SbPh <sub>3</sub> ) <sub>3</sub>	2 <b>75(s)</b>	470(m),1010(s), 1060(s),1420(s)	450(m)	670(w),690(w),730(s),990(s), 1180(m),1290(m),1470(s).
5. ~	RuCl <sub>2</sub> (AsMePh <sub>2</sub> ) <sub>3</sub>	270(w),33	O(m)	480(s)	685(s),730(m),740(sn),835(m), 990(w),1420(s),1470(m)
6.	RuCl <sub>2</sub> (AsMe <sub>2</sub> Ph) <sub>3</sub>	235(m),31	5(s)	425(m),475	<pre>(m) 590(s),685(s),720(s),845(s), 875(s),1020(s),1070(s), 1230(s),1385(m),1475(s).</pre>
7.	RuCl <sub>2</sub> (SbPh <sub>3</sub> ) <sub>3</sub>	260(w),27	5(m)	455(m), 465(m)	650(m),675(m),710(s),985(w), 1050(w),1420(s),1470(s).
8.	RuC12(DPAM)2	230(m),27	0(s)	330(s), 485(s)	585(m),615(m),690(s),735(s)
2.	RuCl <sub>2</sub> (DPPM)2	230(m),27	5(s)	510(s) 545(m)	620(m),690(m),710(m),740(m), 775(s)
10.	Pucl <sub>2</sub> (DPPE) <sub>2</sub>	320(m)		510(s) 530(v.s)	660(w),690(s),715(s),730(m), 740(m)
11.	Ruci <sub>2</sub> (dPAE) <sub>2</sub>	320(m)		450(m), 460(s) 500(s) 540(m)	565(m),610(w),690(v ·s)730(v ·s) 740(v ·s)

Table 3. IR spectra of ruthenium(II) complexes (3000-200 cm<sup>-1</sup>)

Table 4. Proton NMR spectra of ruthenium(II) complexes\*

S.No.	Complex	Phenyl protons	Methyl protons	Methylene protons	Methyl/Methylene protons
1.	RuCl <sub>2</sub> (DMSO) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>				•
	(Brown) (Green	2•15(m) 2•65(m) 3•60(m)	6.55(m) 7.75(m) 8.80(m)		
2.	RuCl <sub>2</sub> (DMGO)(AsMePh <sub>2</sub> ) <sub>3</sub>	2.80(m)	8.30(m) 8.75(m)		L.20(m) 5.30(m) 6.50(m)
3.	$\operatorname{RuCl}_2(\operatorname{DMSO})(\operatorname{AsMe}_2\operatorname{Ph})_3$	2.55(m)	8.13(m),8.57(m)		6.69(m),7.10(m)
<b>*</b> •	RuCl <sub>2</sub> (DMSO)(SbPh <sub>3</sub> ) <sub>3</sub>	1.75(m),2.76(m)	6.50(m)		
5.	RuCl <sub>2</sub> (AsMePh <sub>2</sub> ) <sub>3</sub>	2.50(m),2.90(m)	8.30(m),8.65(m)		
é.	RuCl <sub>2</sub> (AsMe <sub>2</sub> Ph) <sub>3</sub>	3.90(m),3.97(m)	8.70(m),8.97(m)		
Z:	RuCl <sub>2</sub> (SbPh <sub>3</sub> ) <sub>3</sub>	3.70(m),4.00(m)			
Å.	RuCl <sub>2</sub> (DPAM) <sub>2</sub>	3.30(br),3.95(mbr)		5.87(d)	
2:	RuCl <sub>2</sub> (DPPM) <sub>2</sub>	3 <b>.96(m)</b>		5.80(d),8.70(t)	
19:	RuCl <sub>2</sub> (DPPE) <sub>2</sub>	<sup>1</sup> +•10(m)		7.26(m),8.47(m)	
11.	RuCl <sub>2</sub> (DPAE) <sub>2</sub>	4.10(m)		7.80(s),8.63(s)	

(\*) Jvalues: S = singlet; d = doublet; t = triplet; b = broad; m = multiplet.

respectively. The  $n - \pi^*$  transition undergoes a red shift in the sulphur coordinated complex and is exhibited at 230 nm ( $\epsilon 2.8 \times 10^4$ ) in the brown complex. The electronic spectrum of triphenylarsine shows absorption bands at 215 and 248 nm assigned to  $\sigma - \sigma^*$  and  $n - \pi^*$  transitions.

These bands are considerably red-shifted in the coordinated arsine at 250 and 270 nm, respectively with an increase in intensity. The absorption band at 290 nm in (1) appears to be a metal ligand (DMSO) charge transfer band. The transitions at 410 and 520 nm can be assigned to d - d transi-

S.No.	Comp lex	Absorption (nm)	入 max (cm <sup>~1</sup> )	E(M1 <sup>-1</sup> Cm <sup>-1</sup> )	Assignment
1.	RuCl <sub>2</sub> (DMSO) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>	230	43478	2.831x10 <sup>4</sup>	С.т.
		250	40000	2.6506110	C.T.
		270	37037	1.6867x10.	C.T.
		290	34402	7.0313X10°3	
		520	19230	2.4024x102	$1A_1 \longrightarrow IT_1^2$
2.	RuCl_(DMSO)(AsMePh_)	230	43478	2.3248x10	C.T.
m	2 23	246	40650	1.1908x10	C.T.
		264	37878	1.8471x10	C.T.
		302	33112	9 • 7741X10°	14
		300	20000	8,5987+102	<b>1</b>
		640	15625	4.44162x10 <sup>2</sup>	$1A_1 \rightarrow 1T_1$
3.	RuCl_(DMSO)(SbPh_)	230	43478	4.6666x10	C.T.
5	2,	250	40000	3 .1250x10	C.T.
		272	36764	2.2083x10	C.T.
		302	33112	2.000x10	C.T.
		580	19685	3 • 73134x10 <sup>2</sup>	$1A_1 \rightarrow 1T_1^2$
4.	BuCl . (AsMePh	252	29682	1,26903+104	с.т
n	2.3	265	32235	1.16279x104	Č.T.
		30 <b>2</b>	33112	7.0778x10-3	C.T.
		370	27027	1.11223x19 <sup>-</sup>	1A,
		510	19607	4.0444x10 <sup>2</sup>	$1A_1 \longrightarrow 1B_2$
		705	14104	1.70946210	$1A_1 \rightarrow 1A_2$
5.	BUCL (ShPh.).	263	38022	2,3342+102	С. <b>т</b> .
in .	1.4012(2011.3/3	298	33557	2.71167 10	C.T.
		303	33003	2.12063x10	C.T.
		434	22988	8.67550x105	
		540	18518	8.01320x105	1A -> 1B
		770	12907	1.42838x10-	1A1 -> 1A2
6.	RuCl_(DPPE)	240	4 1666	2 .29532x10 <sup>4</sup>	C.T.
m	2	250	40000	2 41228x10 <sup>4</sup>	C.T.
		312	32051	2.04670x103	C.T.
		372	26881	1.02309x102	14 1T.
		440	22727	1.00847x10 <sup>2</sup>	$i\hat{\mathbf{x}}_1^1 \rightarrow i\hat{\mathbf{x}}_1^2$
~		245	1.0816	2 22027-104	
m	740-2(Dr. A.B.)2	279	281-16	2 . 10870-10	C.T.
		178	26455	5.42850-102	U • T • 1 & 4T
		432	23148	3.29000x10 <sup>2</sup>	12 3 172
			-•	J ,	··· · · · ·

Table 5. Electronic spectra of ruthenium(II) complexes

\*C.T. = charge transfer bands.

tions in the complex corresponding to  $1A_1 \rightarrow 1T_2$ and  $1A_1 \rightarrow 1T_1$ , respectively. The 10 Dq value calculated from these transitions comes to 20,518 cm<sup>-1</sup>.

Carbonylation of complex (1) (brown isomer) resulted in the formation of the *cis*-dicarbonyl complex (13) by the displacement of a coordinated DMSO and triphenylarsine groups. The displacement is expected on the basis of the high *trans*-effect of DMSO and the arsine groups. The formation of the *cis*-dicarbonyl is indicated by the appearance of strong peak at  $2010 \text{ cm}^{-1}$  accompanied by a peak of medium intensity at 1985 cm<sup>-1</sup> corresponding to the carbonyls *trans* to arsine and DMSO groups, respectively.

Hydrogenation of (1) (brown isomer) resulted in the formation of hydride (23) which exhibited a strong M-H peak around 1960 cm<sup>-1</sup>. The hydride is formed by the displacement of a coordinated chloride by hydride. The IR absorption bands corresponding to DMSO and triphenylarsine in complex (1) remain intact in the hydrido complex. On passing molecular nitrogen through the solution of the hydrido complex a hydrido-dinitrogen complex (26) is formed, as indicated by the total disappearance of metal-halogen band and the appearance of the characteristic dinitrogen peak around 2150 cm<sup>-1</sup>; the hydrido peak was observed at 1940 cm<sup>-1</sup> in the complex. The hydrido and dinitrogen stretching frequency in this complex are similar to those observed in the complex RuH<sub>2</sub>(N<sub>2</sub>)(PPh<sub>3</sub>).<sup>18</sup>

Treatment of complex (1) with nitric oxide resulted in the formation of  $RuCl_2(NO)(DMSO)$ (AsPh<sub>3</sub>)<sub>2</sub> which showed a strong absorption band characteristic of coordinated nitrosyl at  $1850 \text{ cm}^{-1}$ . The NO frequency in this complex could be compared to other ruthenium nitrosyl complexes where NO may be considered to be coordinated as  $NO^{+19}$ .

Six coordinate complexes of the type RuCl<sub>2</sub>-(DMSO)L<sub>3</sub>, (L=AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph, SbPh<sub>3</sub>)

Complexes (2-4) were obtained by the displacement of one weakly O-bonded and two S-bonded dimethylsulphoxide groups from RuCl<sub>2</sub>(DMSO)<sub>4</sub> by the tertiary arsine or stibine. The remaining DMSO group is S-bonded in these complexes as confirmed by the presence of a strong band in the IR spectra of the complexes around 1075 cm<sup>-1</sup> and the absence of bands around 900 cm<sup>-1</sup> which could be assigned to O-bonded DMSO group. Since tertiary arsine and DMSO absorb in the region 400-500 cm<sup>-1</sup>, the band at  $480 \text{ cm}^{-1}$  could not be assigned to either of these alone. The vM-Cl frequency in complexes (2-4) appear as a single peak at 324, 330 and 275 cm<sup>-1</sup>, respectively, indicating a trans geometry of the coordinated chlorides. The complexes have very low dipole moments (0.77 and 1.15 Debye units for complexes 2 and 3, respectively) and are non-conducting in DMA (Table 1).

In complex (2) the phenyl protons of methyldiphenyl arsine merge and appear as a broad multiplet centered at 2.8 $\tau$ . The methyl protons appear as two multiplets of 1:2 intensity at 8.3 $\tau$ and 8.75 $\tau$ , respectively and can be assigned to *meridional* arsines. The methyl protons of DMSO appeared at a lower field than the methyl protons of arsine (between 4.2 $\tau$  and 6.5 $\tau$ ). The multiplets of methyl protons may be explained on the basis of a long range spin interaction of the methyl protons of DMSO with the methyl protons of arsine and vice versa.

The NMR spectrum of complex (3) is very well resolved as far as methyl protons are concerned, the phenyl protons again merge to give a broad multiplet centred at 2.55 $\tau$ . The methyl protons of the *meridionally* disposed dimethylphenylarsine ligand are observed as two multiplets of 1:2 intensity at 8.13 $\tau$  and 8.57 $\tau$ . The methyl protons of DMSO are exhibited as multiplets centred at 6.69 $\tau$ . The integration of NMR spectra are consistent with the proposed formulations.

The phenyl protons of triphenylstibine are well resolved (Table 3) in the NMR spectrum of complex (4) and appear as two multiplets at  $1.75\tau$  and  $2.76\tau$  in the ratio of 1:2. The methyl protons of DMSO appear at  $6.5\tau$ . The probable structure for





these complexes is given in Fig. 3. The complexes have *meridional* disposition of arsine or stibine ligands with *trans* chlorides and conform to  $C_{2\nu}$  symmetry.

The electronic spectra of complexes (2) and (4) (Table 4) show ligand-to-metal charge transfer bands due to DMSO and methyldiphenyl arsine or triphenylstibine. The absorption bands appear around the same region as in complex (1). Thus absorption at 230 nm could be assigned to ligand-metal charge-transfer in DMSO and bands at 246, 264 nm and 250, 272 nm in complexes (2) and (4) respectively may be assigned to ligand-metal charge-transfer in the arsine and stibine ligand, respectively. The absorption bands at 302 nm may be due to metal-ligand (DMSO) charge-transfer bands. The transitions around 400 and 500 nm can be assigned to d-d transition in the complex corresponding to  $1A_1 \rightarrow 1T_2$  and  $1A_1 \rightarrow 1T_1$ transitions, respectively. The 10 Dg value of complexes (2) and (4) calculated from these transitions are 21,067 and 20,861  $\text{cm}^{-1}$ , respectively.

Cis-dicarbonyls (13-15) were obtained from complexes (2-4) by the displacement of DMSO and one of the arsine or stibine groups. The dicarbonyls were confirmed by the appearance of peaks around  $2010 \text{ cm}^{-1}$  and  $2200 \text{ cm}^{-1}$ , 1950 and  $2010 \text{ cm}^{-1}$ , 1980 cm<sup>-1</sup> and  $2040 \text{ cm}^{-1}$  respectively in complexes (13-15).

Reaction of complexes (2) and (3) with molecular hydrogen yielded hydrido complexes (22) and (23) by the displacement of a coordinated chloride by a hydride. The hydrides Ru(H)Cl(DMSO)(AsMePh<sub>2</sub>)<sub>3</sub> and  $Ru(H)Cl(DMSO)(AsMe_2Ph)_3$ show strong absorption peaks around 1960 and 1920 cm<sup>-1</sup> respectively. No hydride was obtained with complex (4) in accord with a much lower acidity of stibine as compared to arsine ligands. Treatment with nitrogen, of the hydrido complex (22) resulted in the formation of the hydridodinitrogen complex (26). The characteristic dinitrogen peak appeared at 2150 cm<sup>-1</sup> and the hydrido peak at 1960 cm<sup>-1</sup>. The other hydrides failed to react with molecular nitrogen.

When nitric oxide was passed through complexes (2)-(4), nitrosyl complexes (28)-(30) were obtained. The NO stretching frequency appeared at 1810 and 1850 cm<sup>-1</sup> respectively in complexes (28)-(30). Nitric oxide with high *trans*-effect prefers to be in a *trans* position to a ligand with a low *trans*-effect. Hence it could not occupy a position *trans* to DMSO. A position *trans* to tertiary arsine or stibine looks more feasible for the ligand which may be considered to be coordinated as NO<sup>+</sup> in these complexes.

Five coordinate complexes of the type  $RuCl_2L_3$ (L = AsMePh<sub>2</sub>, AsMe<sub>2</sub>Ph or SbPh<sub>3</sub>)

These three complexes (5)-(7) were obtained by the interaction of ruthenium blue solution with methyldiphenyl arsine, dimethylphenylarsine or triphenylstibene. Molecular weights of the these complexes in nitrobenzene indicated them to be monomers. The presence of two bands in vM-Cl region at 270,  $330 \text{ cm}^{-1}$  in complex (5) 235 and  $315 \text{ cm}^{-1}$  in complex (6) and 260 and 275 cm<sup>-1</sup> in complex (7) (Table 3), shows two cis chlorides in these complexes. There are many bands in the region 425–490 cm<sup>-1</sup> assigned to vM-L vibrations (L = As or Sb). The complexes are diamagnetic. Two structures may be considered for these complexes; a square pyramid with cis chlorides and two mutually trans and a cis arsine (Fig. 4a) and a trigonal bipyramid with two axial and one equatorial arsine (Fig. 4b). The two proposed structures cannot be distinguished on the basis of NMR since arsines have the same environment in both the structures. For both the structures one should observe in the NMR spectra two singlets of 1:2 intensity due to methyl protons of two arsine groups. Because of cis interactions with equatorial arsines, two multiplets of 1:2 intensity are observed at  $8.3\tau$  and  $8.65\tau$  in complex (5) and  $8.75\tau$ and  $8.97\tau$  in complex (6), respectively. Likewise, phenylprotons also appear as two multiplets at 2.5 $\tau$  and 2.9 $\tau$  and 3.9 $\tau$  and 3.97 $\tau$ , respectively. In a similar manner the NMR spectrum of complex (7) shows multiplets in a 1:2 ratio at 3.7 $\tau$  and 4.1 $\tau$ .

A square pyramidal arrangement of ligands with two *cis* chlorides and a *meridional* arrangement of ligands however seems to be a much better arrangement from a steric view point than the trigonal bipyramidal arrangement. Based on a square pyramidal arrangement of the ligands three spinallowed transitions are possible,  $1A_1 \rightarrow 1A_2$ ,  $1A_1 \rightarrow 1B_2$ ,  $1A_1 \rightarrow 1E_1$ , the first transitions  $1A_1 \rightarrow 1A_2$ should give the 10 Dq value approximately and it is 14,000 cm<sup>-1</sup> in complex (5).

The electronic spectrum of complex (7) shows three d-d transitions at 770, 540, 434 nm which can be assigned to the transitions  $1A_1 \rightarrow 1A_2$ ,  $1A_1 \rightarrow 1B_2$ and  $1A_1 \rightarrow 1E_1$  in a square pyramidal configuration as in complexes (5) and (6). The bands at 263, 298 and 303 nm are charge-transfer bands as in complexes (5) and (6). Based on the lowest energy transitions  $1A_1 \rightarrow 1A_2$  the 10 Dq value in this complex is 12,987 cm<sup>-1</sup>. Complex (7) reacted with carbon monoxide to yield a monocarbonyl (16) which exhibits a single strong band at 1950 cm<sup>-1</sup>.

Complex (5) reacted with molecular hydrogen to yield a hydrido complex (24). As in the other hydrido complexes (21)–(24) complex (24) is formed by the displacement of a chloride from complex (5). The hydride exhibits a strong peak at  $1920 \text{ cm}^{-1}$ . Complexes (6) and (7) failed to react with molecular hydrogen.

Reaction of complex (5) with nitric oxide yielded the nitrosyl complex (31) which showed a strong band around 1910 cm<sup>-1</sup> corresponding to a coordinated NO<sup>+</sup> in this complex.

#### Cis-RuCl<sub>2</sub>(DPAM)<sub>2</sub>

The complex was obtained from  $RuCl_2(DMSO)_4$ by the displacement of all DMSO groups by the chelating agent. Mague and Mitchener<sup>9</sup> had prepared the complex *trans*-RuCl<sub>2</sub>(DPAM)<sub>3</sub> by the interaction of hydrated ruthenium trichloride with excess of DPAM. In this complex, one of the



DPAM was reported to be bidentate and the other two monodentate.<sup>9</sup> The complex reported in this work was thus obtained from a different route and is different in composition and structure from that reported by Mague and Mitchener.<sup>9</sup> The absence of DMSO peaks in the IR spectrum is an evidence of complete displacement of DMSO from  $RuCl_2(DMSO)_4$ . Thus the ligand DPAM seems to act as a bidentate ligand. The peaks at 330 and 485 cm<sup>-1</sup> may be assigned to vM–As vibrations of the coordinated diarsine. The complexes with chelated DPAE or DPAM lack a centre of symmetry in the molecule and diarsine groups are coordinated as cis or trans and more than one vM-As stretching frequency are observed. The cis or trans geometry in these complexes is based mostly on the observed vM-Cl stretching frequency. The bands at 230 and 270  $cm^{-1}$  in complex (8) may be associated with the M-Cl vibrations of the cis chlorides in the complex. The M--Cl frequencies are lower than complexes with trans-halogen since in this case the chlorides are trans to arsenic. A cis disposition of the two arsines in the complex is confirmed by the NMR spectrum which shows methylene protons as a doublet at  $5.06\tau$ . The doublet arises due to two non-equivalent methylene protons of a chelated diarsine group. The position of methylene resonance at  $8.7\tau$  is in accord with the bidentate coordination of DPAM. In the complex  $RuCl_2(DPAM)_3$  the peaks due to the methylene protons of bidentate diarsine molecule were observed<sup>9</sup> at  $5.17\tau$  and those due to monodentate diarsine at  $7.28\tau$ . The arrangement of a chelated diarsine is thus in accord with the earlier observations.<sup>9</sup> There are two groups of phenyl protons one due to two mutually trans diarsine and another one due to two mutually cis diarsine groups. These two groups give rise to a complicated  $A_2B_2$  pattern where many of the peaks overlap and appear as a broad multiplet centred at 3.5 $\tau$  and many peaks in the 3.95–4.43 $\tau$  region. Integration of phenyl and methylene protons however is in agreement with the proposed formulation of the complex. The probable structure for the complex is given in Fig. 5.

The electronic spectrum of  $\text{RuCl}_2(\text{DPAM})_2$ show ligand-metal charge-transfer bands at 245 and 270 nm (Table 5). The *d*-*d* transition in the complex was observed at 460 nm which can be assigned to the  $1A_1 \rightarrow 1T_2$  transition.

Carbonylation of the complex yielded a dicarbonyl  $RuCl_2(CO)_2$ -(DPAM)<sub>2</sub> (17). The IR spectrum of the dicarbonyl shows strong bands at 1935 and 2000 cm<sup>-1</sup> associated with *cis* dicarbonyls. The dicarbonyls may be considered to have formed by



the opening of the DPAM chelate ring resulting in two molecules of DPAM acting as monodentate ligand. Mague and Mitchener<sup>9</sup> have prepared the compound  $RuCl_2(CO)_2(DPAM)_2$  by the interaction of  $RuCl_2(DPAM)_3$  with carbon monoxide. The configuration of the compound was proposed

to be a mixture of (a) and (b) in Fig. 6. The compound  $RuCl_2(CO)_2(L)_2$  obtained in this investigation from *cis*-RuCl\_2(DPAM)<sub>2</sub> is expected to have configuration 6(b) since carbonylation is expected to open the bidentate chelate rings of DPAM without any rearrangement of the halogens



which is necessary in forming 6(a). The carbonyl frequencies of 2000 and 1930 cm<sup>-1</sup> are in accord with a *cis* disposition of carbonyl groups to halogens.

#### Cis-RuCl<sub>2</sub>(DPPM)<sub>2</sub>

This complex is also prepared from RuCl<sub>2</sub>(DMSO)<sub>4</sub> and diphos as other bidentate diphosphine or diarsine complexes. A complex of similar composition trans RuCl<sub>2</sub>(DPPM), was earlier reported by Chatt and Hayter<sup>8</sup> and later by Mague and Mitchener.<sup>9</sup> The former workers<sup>8</sup> prepared the complex directly from hydrated ruthenium trichloride and DPPM and the latter from red ruthenium carbonyl solution and DPPM. In this complex, the ligand is coordinated as a bidentate group. The procedure employed in this work for the preparation of RuCl<sub>2</sub>(DPPM)<sub>2</sub> is more convenient than the earlier methods and gives the cis compound in a higher yield than the trans compound. As in the case of interaction of other chelated ligands with RuCl<sub>2</sub>(DMSO)<sub>4</sub> interaction of DPPM with RuCl<sub>2</sub>(DMSO)<sub>4</sub> results in complete displacement of DMSO by chelated phosphine as indicated by absence of peaks corresponding to coordinated DMSO in the IR spectrum of the complex.

The peaks at 420, 510,  $545 \text{ cm}^{-1}$  were assigned to vM-P vibrations of coordinated disphosphines (Table 3). The bands at 230,  $275 \text{ cm}^{-1}$  were indicative of a *cis* geometry for the chlorides.

The NMR spectrum of complex 9 exhibits peaks of equal intensity for methylene protons at  $5.8\tau$ and 8.7 $\tau$ . This could be assigned to a bidentate and a monodentate phosphine ligand. On the basis of two modes of coordination for the complex, there are two structures possible for the complex. One is square pyramid (Fig. 7a) with two mutually cis phosphorus, a trans phosphorus and two mutually cis chlorides and the other one is a trigonal bipyramid (Fig. 7b) type of structure in which two phosphorus atoms (of two ligands) and a chloride are equitorial and a phosphorus and chlorine in axial position. In both the cases, there are two non-equivalent methylene groups due to the two modes of coordination of the ligand and two peaks due to methylene protons are expected in the NMR spectrum. Phenyl protons appear as a broad multiplet centered at  $3.96\tau$ . As in the case of other five coordinate complexes (5)-(7), the NMR as well as the electronic spectra of the complexes cannot decide between the two possibilities. On steric grounds the square pyramidal arrangement (7a) seems to be a better possibility than the trigonal bipyramid (7b).



On carbonylation of (9), a cis-dicarbonyl of RuCl<sub>2</sub>(DPPM)<sub>2</sub> is formed which shows strong bands at 1960 and 2000  $\text{cm}^{-1}$ . As in the case of (8), the dicarbonyl formation may involve the rupture of a bidentate chelate ring and as such has two monodentate ligands in trans disposition as that of RuCl<sub>2</sub>(CO)<sub>2</sub>(DPAM)<sub>2</sub>. The carbonylation of  $RuCl_2(DPPM)_2$  can be expected to be more facile on the basis of a square pyramidal configuration rather than a trigonal bipyramid (Fig. 8a). In the former case one of the carbons monoxide molecules can add to the vacant coordination position on the metal ion and the other opens up the chelated DPPM groups to form  $RuCl_2(CO)_2(DPPM)_2$ . trigonalbipyramidal structure requires re-A arrangement of various groups. Mague and Mitchener<sup>9</sup> have reported a cationic monocarbonyl species [RuCl(CO)(DPPM)<sub>2</sub>]Cl by the interaction of trans-RuCl<sub>2</sub>(DPPM)<sub>2</sub> with carbon monoxide (Fig. 8b). In this case the displacement of a chloride seems to be easier than rupture of a DPPM group to form the carbonylated complexes. The formation of a dicarbonyl or monocarbonyl thus seems to depend very much on the geometry of the starting material.

Complex (9) reacted with nitric oxide to yield a nitrosyl complex  $RuCl_2(NO)(DPPM)_2$  (32). The formation of a nitrosyl complex is confirmed by the appearance of a single band around 1825 cm<sup>-1</sup>. A nitrosyl group gets added to the vacant coordi-



Fig. 8.

nation position on the metal ion to give a six coordinated species.

#### RuCl<sub>2</sub>(DPPE)<sub>2</sub> and RuCl<sub>2</sub>(DPAE)<sub>2</sub>

These two complexes were prepared by the reaction of RuCl<sub>2</sub>(DMSO)<sub>4</sub> with chelated phosphine or arsine. The complex RuCl<sub>2</sub>(DPPE)<sub>2</sub> was previously obtained by Chatt and Hayter<sup>8</sup> by the direct reaction of hydrated ruthenium trichloride ethanol with DPPE and the complex in RuCl<sub>2</sub>(DPAE)<sub>2</sub> was synthesized by Mague and Mitchener<sup>9</sup> by the reaction of  $Ru(CO)_n Cl_3$  with DPAE. The method adopted in this work is different and more convenient than those of previous investigations<sup>8,9</sup> and gave a higher yield of the complexes. All the four DMSO groups from RuCl<sub>2</sub>(DMSO)<sub>4</sub> are replaced by the bidentate chelating ligands to form  $RuCl_2L_2$  (L = DPPE or DPAE). This is confirmed by the absence of peaks due to coordinated DMSO in the IR spectra of these complexes. The bands in the region 400–500 cm<sup>-1</sup> may be assigned to the coordinated phosphorus or arsenic. The trans configuration of the complexes is confirmed by a single vM-Cl peak at  $320 \text{ cm}^{-1}$  in both the complexes.

The *trans* geometry of the chloride groups allow only *trans* disposition of the bidentate ligand. This fact is confirmed by the NMR spectra of the two complexes. The NMR spectrum of the complex  $RuCl_2(DPPE)_2$  shows a multiplet at 4.1 $\tau$  due to the phenyl protons of the phosphine. The peaks due to the methylene protons are observed as multiplets at 7.26 $\tau$  and 8.47 $\tau$  in a ratio of 1:2. The methylene protons in the chelated ligand do not seem to be equivalent because in the five membered chelate ring methylene protons are expected to be above and below the plane containing the metal ion and the two phosphorus atoms. The configuration of the protons seems to be fixed in the ring since a flip-flop mechanism would give rise to a single methylene peak. The methylene triplet is expected because of the spin coupling of the protons by <sup>31</sup>P. In the NMR spectrum of the free ligand, the methylene protons are observed as one triplet at 8.07 $\tau$ . This triplet arises due to splitting of equivalent methylene proton peak by the two phosphorus atoms. The NMR spectrum of complex RuCl<sub>2</sub>(DPAE) shows a similar pattern to RuCl<sub>2</sub>(DPPE). The only difference is that the methylene protons appear as two singlets since there is no splitting by arsenic. In the free ligand also there is a singlet due to equivalent methylene protons. The phenyl protons merge together and appear as a broad multiplet centered at  $4.1\tau$  in the complex. The integration of the phenyl and methylene protons in the two complexes is consistent with the proposed structures for these complexes (Fig. 9).

The electronic spectrum of  $RuCl_2(DPPE)_2$  gave the ligand-metal charge-transfer bands at 240 and



250 nm (Table 5). The d-d transitions in the complex are observed at 372 and 440 nm which can be assigned to  $1A_1 \rightarrow 1T_2$  and  $1A_1 \rightarrow 1T_1$  transitions, respectively. The 10 Dq value calculated for the complex is 23,770 cm<sup>-1</sup>. The electronic spectrum of RuCl<sub>2</sub>(DPAE)<sub>2</sub> gave ligand-metal charge-transfer bands at 245 and 260 nm. These charge-transfer bands can be compared to the monoarsine (Table 5) complexes that give bands around 240-250 and 260-270 nm. These bands may be assigned in a manner similar to other spin paired octahedral complexes as (10). The 10 Dq value calculated for the complex is about 23,935 cm<sup>-1</sup>. On comparing the 10 Dq value calculated for the chelating phosphine and arsine complexes to those of nonchelating arsine and DMSO complexes, it may readily be seen that chelation gives a much higher 10 Dq values (about 400 cm<sup>-1</sup> more than nonchelated compounds). This indicates extra stability and much higher ligand field strength of the chelated ligands as compared to the monodentate ligands.

Carbonylation of complexes (10) and (11) yielded the monocarbonyls (19) and (20), respectively. These carbonyls can be considered to be cationic species obtained by the displacement of a coordinated chloride from the coordination sphere of the metal ion. The monocarbonyls (19) and (20) exhibit single sharp peaks at 1950 and  $1925 \text{ cm}^{-1}$ , respectively. The complexes are cationic as indicated by their conductivities in DMA (1:1 electrolyte). Displacement of carbon monoxide from  $Ru(CO)_2Cl_n$  by DPAE gives rise to RuCl<sub>2</sub>(DPAE)<sub>2</sub>.<sup>9</sup> The coordination of DPAE or DPPE to the metal ion seems to be stronger than carbon monoxide since the chelating ligands can displace carbon monoxide from the coordination sphere of the metal ion. In the case of complexes (10) and (11) however a coordinated chloride is displaced in the presence of excess of carbon monoxide from the coordination sphere of the metal ion to form cationic monocarbonyl species. These cationic carbonyl complexes are prepared for the first time and their formation seems to be a general phenomenon in the reactions of chelated phosphine or arsine complexes with carbon monoxide.

Complex  $RuCl_2(DPAE)_2$  reacted with nitric oxide yielding a nitrosyl complex  $RuCl_2(NO)$  $(DPAE)_2$  (33). The nitrosyl group shows a band at  $1825 \text{ cm}^{-1}$  in the complex. The nitrosyl formation may involve the rupture of a bidentate chelate ring and as such may have bidentate and monodentate DPAE ligand and a seven coordinate geometry for ruthenium.

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