

## NOTE

**Reactions of Dichlorotris (Triphenylphosphine) Ruthenium(II) with Various Sulfur Ligands**

M.G. BHOWON\* and H. REEDOY

Department of Chemistry

Faculty of Science, University of Mauritius, Reduit, Mauritius

Reactions of dichlorotris (triphenylphosphine) ruthenium(II) with various sulfur ligands such as *m*-(mercaptoacetamido) phenol *m*-(MAP), thioacetamide, cyanothioacetamide have been described. These compounds were characterized by analytical, magnetic and spectroscopic (UV, Vis, IR) data.

Dichlorotris (triphenylphosphine) ruthenium(II) is an invaluable precursor of many ruthenium(II) complexes and can undergo a variety of substitution reactions<sup>1,2</sup>. Recently many investigations are carried out on  $[\text{RuCl}_2(\text{PPh}_3)_3]$  because it is a very efficient catalyst for many organic and inorganic reactions<sup>3,4</sup>. Many reactions of dichlorotris (triphenylphosphine) ruthenium(II) with the ligands having the donor atoms such as oxygen, nitrogen and few with sulfur are reported in literature. The present study is undertaken with a view to prepare and investigate the reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  with different sulphur ligands.

All chemicals used were of AR grade. Triphenylphosphine, cyanothioacetamide, thioacetamide were purchased from BDH while  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  from Aldrich. *m*-(mercaptoacetamido) phenol (*m*-MAP)<sup>5</sup> and dichlorotris (triphenylphosphine) ruthenium(II)<sup>6</sup> was prepared by standard literature method.

Infrared spectra were recorded on Mattson 1000 FTIR spectrophotometer in the range 4000–400  $\text{cm}^{-1}$ . Electronic spectra were recorded on an ATI Unicam 8700 in the range 200–700 nm. Magnetic susceptibilities were measured on a Sherwood scientific balance. Microanalyses were performed at the Imperial College, London.

**Reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  with *m*-(MAP)**

(1) Reaction of  $\text{Ru}(\text{m-MAP})_2(\text{CH}_3\text{OH})_2$  was prepared by refluxing in *m*-MAP and  $\text{RuCl}_2(\text{PPh}_3)_3$  in methanol for 10 h. The solution was then concentrated and the resulting oil was washed with  $\text{CH}_2\text{Cl}_2$ , ether, THF and then dissolved in methanol followed by addition of ether resulting in a black compound A. The product was recrystallised from methanol/ether and dried *in vacuo*.

(2) Reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  with L (L = thioacetamide, cyanothioacetamide). In a stirred solution of  $\text{RuCl}_2(\text{PPh}_3)_3$  in dichloromethane was added a solution of

ligand (ratio of 1:1 and 1:2) in methanol. The reaction mixture was refluxed for 3 h. On concentrating the resulting solution on water bath, green microcrystalline compound B was filtered off and washed with ether. Compounds C, D and E were obtained upon addition of ether which was separated by filtration and washed with dichloromethane and ether. Compounds were further recrystallised with methanol/ether and dried in vacuo.

Reactions of the complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with the ligands (*m*-MAP, thioacetamide, cyanothioacetamide) in methanolic solvent led to the formation of substituted complexes. Table-1 lists their empirical formulae, microanalytical data (given therein) together with some of their physical properties. These are air stable, green and black solids, soluble in DMSO,  $\text{CH}_2\text{Cl}_2$  etc. but are insoluble in acetone, THF and benzene.

TABLE-1  
MAGNETIC MOMENT, MELTING POINT AND ANALYTICAL DATA  
FOR COMPLEXES

Compounds/Colour	m.p. (°C)	Analysis % Found (Calcd.)				$\mu_{\text{eff}}$ (B.M.)
		C	H	N	Cl	
Ru( <i>m</i> -MAP) <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub> A, Black	>350	40.2 (40.8)	4.2 (4.5)	4.8 (5.3)	— —	Diamagnetic
RuCl <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> (SCNH <sub>2</sub> CH <sub>3</sub> ) B, Green	182–186	56.8 (56.5)	4.6 (4.3)	1.5 (1.7)	12.8 (13.2)	1.6
RuCl <sub>2</sub> (PPh <sub>3</sub> )(SCNH <sub>2</sub> CH <sub>2</sub> CN)(CH <sub>3</sub> OH) <sub>2</sub> C, Green	>350	45.8 (46.1)	4.1 (4.5)	4.0 (4.6)	11.2 (11.8)	Diamagnetic
RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (SCNH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> D, Yellowish green	197–201	56.1 (56.7)	4.1 (4.7)	3.0 (3.3)	7.8 (8.4)	Diamagnetic
RuCl <sub>3</sub> (PPh <sub>3</sub> )(SCNH <sub>2</sub> CH <sub>2</sub> CN) <sub>2</sub> E, Green	>350	45.3 (44.2)	3.5 (3.3)	5.5 (4.9)	17.5 (18.7)	1.49

The infrared spectrum of compound A shows disappearance of S—H band ( $2552\text{ cm}^{-1}$ ) and a shift of  $16\text{ cm}^{-1}$  towards higher side in  $\nu(\text{C}=\text{O})$  frequency ( $1649\text{ cm}^{-1}$ ) when compared with the spectrum of free ligand. The disappearance of sharp characteristic bands of triphenylphosphine ( $750\text{--}500\text{ cm}^{-1}$ ) shows the absence of PPh<sub>3</sub> in the complex. Absence of  $\nu(\text{SH})$  and shifting in the frequency of CO in the spectrum indicate the coordination of the metal through sulfur and oxygen.

When the reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  was carried out with  $\text{CH}_3\text{CSNH}_2$  and  $\text{NCCH}_2\text{CSNH}_2$  in the ratio 1:1 and 1:2, B, C, D, E were obtained respectively.

In all the complexes the band due to  $\nu(\text{C}=\text{S})$  at  $1269\text{ cm}^{-1}$  in the free ligands was shifted to lower wave number showing coordination of ligand to ruthenium through sulphur. But the shifted band was difficult to identify because of the overlapping with the characteristic sharp triphenylphosphine bands in the region ( $1487\text{--}523\text{ cm}^{-1}$ ). A medium intensity band present in C and E at  $2201\text{--}2185\text{ cm}^{-1}$  corresponds to  $\nu(\text{C}\equiv\text{N})$ . In all the complexes bands around  $3500\text{--}3400\text{ cm}^{-1}$  are due to  $\nu(\text{N—H})$  and at  $1620\text{--}1580\text{ cm}^{-1}$  due to deformation vibration of  $\text{NH}_2$ .

The visible spectra of the complexes exhibited a rather broad band around 450–420 nm. Since it is generally believed that (MLCT) transition in ruthenium +2 complexes occurs under a broad band around 450–430 nm<sup>7</sup>, a similar band in the electronic spectra of our complexes suggested ruthenium on +2 oxidation state which was also confirmed by magnetic moment (diamagnetic). The electronic spectra of ruthenium(III) complexes showed band at 430 nm and 620–600 nm due to metal to ligand and ligand to metal charge transfer transitions. In all the complexes intense bands or shoulders below 300 nm are  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  intraligand transitions.

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