



Short Communication

Triphenylphosphine Sulphide as a Complexing Agent : Synthesis and Characterisation of Complexes of Rhodium (I) and Ruthenium (II)

Yadav S.N., Kumar Vijay, Singh R.N. and Shubhra Prabha*
P.G. Centre, Department of Chemistry, College of Commerce, Patna-8000 020, INDIA

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Abstract

Rhodium(I) complexes of Wilkinson's catalyst $[Rh(PPh_3)Cl]$ types, have been synthesised and characterised by elemental analysis, IR, 1H NMR, ^{13}C NMR and magnetic measurements. The complexes have been found to be four coordinated with square planar geometry around the Rhodium metal ions with diamagnetic character, while ruthenium metal forms five coordinated with trigonal bipyramid geometry with paramagnetic character.

Keywords: Triphenylphosphine Sulphide, Rhodium (I), Ruthenium (II), Wilkinson's catalyst, complexes.

Introduction

Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ ¹⁻⁴ was first synthesised by Wilkinson in 1965 by heating rhodium chloride $RhCl_3 \cdot 3H_2O$ with triphenyl phosphine in boiling ethanol. It is a square planar complex having three bulky triphenylphosphine ligands. Rhodium(I) complexes of the types $[Rh(CO)LL(PPh_3)_2]$ have been synthesised and characterised by K. Natrajan⁵ et. al. and proposed the structure on the basis of elemental analysis, IR, ^{31}P NMR and electronic measurements. Hydridophosphine complexes of rhodium and ruthenium have been synthesised and characterised Rh. $H[(C_6H_5)_3P]_4$, and $[H Rh(C_6H_5)_3P]$ by Kenneth⁶ et al; some typical phosphine complexes of ruthenium such as $[RuClH(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$ $[Ru(CO)_3(PPh_3)_2]$ $[Ru(acac)_2(PPh_3)_2]$ $[Ru(C_2H_4)(PMe_3)_4]$ $[RuH_2(PMe_3)_4]$ ⁷ etc. have been already known. A number of metal complexes of $Ru^{(II)}$ and $Rh^{(I)}$ with mixed ligand complexes of composition $[Ru(CO)(LL)(PPh_3)_2Cl]$ and $[RuH(CO)(LL)(PPh_3)_2]$ $[Rh(CO)(LL)(PPh_3)_2]$ and $[Rh(LL)(PPh_3)_3]$ have been synthesised and characterized by elemental analysis, IR and electronic spectral measurements by K. Natrajan⁸ et. al. where LL = β -diketonate/monothio- β -diketonate. Ruthenium complexes of sulphur containing ligands such as $[Ru(SH)(CO)_2(PPh_3)_3]$ ⁹ $[Ru(S_2CNEt_2)_2(PPh_3)_2]$ ¹⁰ have been also synthesised and characterized by various chemists¹¹⁻¹².

In this paper, we have described the synthesis of mononuclear rhodium(I) and ruthenium(II) complexes with triphenylphosphine sulphide ligand in the field of organometallic compounds. The complexes thus prepared have been characterised and structures proposed on the basis of spectral (IR, NMR), magnetic measurements and analytical data.

Material and Methods

The analysis of ligand and its metal complexes with physical measurements (IR, NMR etc.) have been performed from SAIF,

IIT, Powai, Mumbai. The ligand TPPS(L) was prepared by reported methods¹³⁻¹⁴.

Preparation of $[RhL_3Cl]$ complex: 100mg Wilkinson's catalyst was treated with 10ml methanol and benzene mixture 250mg ligand was dissolved in 20ml benzene and were mixed in above solution. The mixture become reddish brown. It was distilled for 3-hours to give required product $[RhL_3Cl]$. It was washed with ethanol and dried in vacuo.

Preparation of $[RuL_3Cl_2]$ Complex: An aqueous alcoholic solution of ruthenium(III) chloride was treated with alcoholic benzene mixture of ligand in 1 : 3 molar ratio. The reaction was distilled for 3-hours to give red required product. The resulting solid was washed with ethanol and dried in vacuo.

Results and Discussion

The complexes of Rh^I and Ru^{II} with triphenylphosphine sulphide (TPPS) ligand were prepared. The colour of these complexes are reddish brown/ red coloured. They are stable in air and are nonhygroscopic. They are slightly soluble in ethanol fairly soluble in DMF as well as in benzene. They are insoluble in water. The compositions of the complexes have been represented as RhL_3Cl and RuL_3Cl_2 . The rhodium(I) complex is found to be diamagnetic while ruthenium(II) is found to be paramagnetic.

Infrared spectra : The ir-stretching strong bands have been found between $3057-3054\text{ cm}^{-1}$ attributed to $\nu(C-H)$ vibrations and the band is not effected appreciably by substituent groups¹⁵. Bands near $1963, 1906, 1827$ and 1775 cm^{-1} are due to substituted benzene ring, as substituted benzene also show speaks in $2000-1670\text{ cm}^{-1}$ region¹⁶. The IR-spectrum of ligand and its metal complexes display medium and weak bands in region $1672-1624\text{ cm}^{-1}$ and $1590-1583\text{ cm}^{-1}$ attributed to carbon-carbon multiple bond stretching vibrations. The ligand and complexes also exhibit a very strong absorption band in the range of $1480-1435\text{ cm}^{-1}$ attributed to phenyl ring skeletal vibrations due to $\nu(C=C)$ and $\nu(C-C)$ vibrations.

Table-1
Characteristic IR frequencies (cm⁻¹) of ligand and complexes

Comp.	$\nu(\text{C-H})$ Phenyl ring	Phenyl ring skeletal vibration				$\delta(\text{C-H})$ and (C-C) vibration	$\nu(\text{P-C})$ stretch	$\nu(\text{P=S})$	Aromatic ring singly substituted		
		$\nu(\text{C=C})$	$\nu(\text{C-C})$								
TPPS	3057	1668	1585	1480	1435	1274	1182	929	754	692	638
[RhL ₃ Cl]	3056	1624	1590	1484	1438	1267	1185	925	754	697	650
[RuL ₃ Cl ₂]	3054	1672	1583	1481	1438	1267	1191	914	745	698	650

The ligand and complexes display medium ir-bands near 1274-1267 cm⁻¹ and strong band near 1191-1182 cm⁻¹ and very strong band at 1087-1069 cm⁻¹ and 929-914 cm⁻¹ region attributed to (C-H) bending, (C-C) stretches and $\nu(\text{C-P})$ vibrations, while (P = S) stretches are observed in the region 1169-1159 cm⁻¹ as a strong and broad band. Which supports the participation of sulphur as donor atom¹⁷. A very strong and broad band also observed in the ligand and complexes at 754-745 cm⁻¹ attributed to $\nu(\text{P = S})$ vibrations. The strong peak at 692 cm⁻¹ and 638 cm⁻¹ indicate the facts that the aromatic ring may be singly substituted¹⁸ as shown in table-1.

NMR spectra : ¹H NMR spectra and ¹³C NMR spectra of these complexes of Rhodium(I) and Ruthenium(II) with TPPS ligand have been recorded in CDCl₃ solvent. Rhodium complex display a number of signals between 7.40 ppm to 7.72 ppm, indicate that a number of benzene rings are present in the complexes. Since the hydrogen atoms directly bonded to an aromatic ring are easily identified by P NMR spectra. These hydrogens are strongly deshielded by the aromatic ring and also absorb between 7.0 to 8.0 ppm downfield from TMS standard. Ruthenium complex also display a number of signals between 7.25 ppm to 7.75 ppm.

¹³C NMR spectra of the Complexes exhibit C₂/C₆, C₃/C₅, C₄ and C₁ type absorption peaks 128.3/128.5, 131.7/131.8, 131.8, 131.9 and 132.0 δ indicating the presence of phenyl rings in the complexes. ¹³C NMR spectra of the both complexes show that the triplet peaks at δ 77. This is the carbon signal for deuterated chloroform (CDCl₃) solvent which split into three equal sized peaks by coupling with the deuterium atom. The spectra of the complex also exhibit absorption between 2.45 to 3.25 δ indicating the presence of electronegative chlorine atom. The ruthenium(II) complex also shows four different types of peaks range between 128-135 δ indicating the presence of phenyl groups as well as formation of Ru-S bond¹⁹⁻²⁰. Organophosphorous compounds formed aryl (C-P) bonds between 125-140 δ according to William Kemp²¹. Both the complexes also formed absorption peaks between above range confirms the presence of (C-P) bonds in the complexes.

Conclusion

In the light of above discussion, particularly the metal-ligand ratio, its analytical data, IR spectra, NMR spectra and magnetic properties of ligand and complexes suggested that rhodium(I) complex is four coordinated square planar geometry, which is

the most favourable geometry of the rhodium(I) complexes, while the ruthenium(II) has trigonal bipyramidal structure. Rh^I complex is found to be diamagnetic, while Ru^{II} complex is paramagnetic.

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