

Organometallic complexes of ruthenium (II) with 3-(4'-Pyridyl)-4-phenyl-triazoline -5-thione

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(Received: January 28, 2009; Accepted: March 10, 2009)

ABSTRACT

Some organometallic complexes of ruthenium (II) have been isolated and characterized on the basis of analytical, magnetic moment and electronic and IR spectral data. Complexes have been assigned octahedral configuration. The nature of shifts and change in intensity of four thioamide bands of 3-(4'-Pyridyl)-4-phenyl-Triazoline-5-thione indicates bonding through thio carbonyl sulphur of the ligand.

Key word: Organometallic Ru(II), complexes, mixed ligands, Triphenyl phosphine and 3-(4'-Pyridyl)-4-phenyl-triazoline-5-thione.

INTRODUCTION

Organometallic derivatives of ruthenium (II) have drawn special attention owing to their catalytic potential¹. Several ruthenium (II) complexes are of importance to their medicinal properties²⁻⁴ and reported to possess activity against viruses, tumors and fungi⁵⁻⁶. The present study describes preparation and characterization of some novel organometallic complexes of ruthenium (II) following our previous report⁷⁻¹⁰.

EXPERIMENTAL

All chemicals used were either chemically pure or AR grade. Solvents were distilled and dried before use. The ligand 3-(4'-Pyridyl)-4-phenyl-Triazoline -5-thione (PPytTH) was prepared by slightly modified method reported in literature⁽¹¹⁾. The precursor complexes $[\text{RuCl}_2(\text{P}f_3)_4]$ ⁽¹²⁾ and $[\text{RuHCl}(\text{CO})(\text{P}f_3)_3]$ ⁽¹³⁾ were prepared by the method reported in literature.

Dihydridodithiocarbonyl bis (triphenyl phosphine) ruthenium (II): $[\text{RuH}_2(\text{CS})_2(\text{P}f_3)_2]$

Suspension of $\text{RuCl}_3 \cdot 4\text{H}_2\text{O}$ (0.5g), CS_2 (10ml), CH_3OH (40ml) and NaOH (2N, 15ml) and Triphenyl phosphine (7g) were stirred on magnetic stirrer for two hours at 85°C. A light grey solid was separated out on cooling. It was filtered, washed with methanol and ether and dried in Vacuo over anhydrous CaCl_2 (Mpt= 81°C) Analysis:

Found (%) : C, 63.2; H, 4.2; Ru, 14.4
Calcd (%) : C, 63.7; H, 4.4; Ru, 14.1

Dihydridodithiocarbonyl triphenyl phosphine 3-(4'-pyridyl)-4-phenyl-triazoline-5-thione ruthenium(II): $[\text{RuH}_2(\text{CS})_2(\text{P}f_3)_2(\text{PPytTH})]$

This complex was prepared using $[\text{RuH}_2(\text{CS})_2(\text{P}f_3)_2]$ and PPytTH in molar ratio 1:1 in benzene. (M.Pt= 101°C).

Analyses

Found %: C, 39.0; H, 3.7; N, 8.0; Ru, 14.3
Calcd (%): C, 38.9; H, 3.8; N, 7.9; Ru, 14.2

Chlorocarbonylhydridotriphenylphosphine Bis{3-(4'-pyridyl)-4-phenyl-Triazoline-5-thione} ruthenium(II): [RuHCl(CO)(Pf₃)(PPyTH)₂]

This deep brown complex was prepared from pink isomer of [RuH(CO)(Pf₃)₃Cl] in benzene as we reported earlier⁽⁷⁾. (M.Pt= 138°C)

Analyses

Found (%): C, 57.8; H, 3.7; N, 12.1; Ru, 11.1,
Calcd (%) : C, 57.7; H, 3.8; N, 11.9; Ru, 10.8,

Chlorocarbonylhydridobis(triphenylphosphine) 3-(4'-Pyridyl)-4-phenyl- Triazoline-5-thione ruthenium (II): [RuHCl(CO)(Pf₃)₂(PPyTH)]

This light yellow complex was prepared from yellow isomer of [RuHCl(CO)(Pf₃)₃] in benzene as reported earlier⁽⁷⁾. (M.pt = 83°C).

Analyses

Found (%): C, 63.6; H, 4.4; N, 6.1; Ru, 10.8
Calcd (%) : C, 63.5; H, 4.3; N, 5.9; Ru, 10.7

Dichlorodithiocarbondi sulphidebis (triphenyl phosphine) ruthenium (II): [RuCl₂(CS₂)₂(Pf₃)₂]

This golden brown complex was prepared starting from Wilkinson compound RuCl₂(Pf₃)₄⁽¹²⁾. Benzene solution of RuCl₂(Pf₃)₄ is suspended in 15 ml carbon disulphide and stirred on magnetic stirrer for two hours and kept over night at room temperature. The golden brown crystals obtained were dried in a vacuum desiccator over anhydrous CaCl₂. (M.Pt = 120°C).

Analyses

Found (%) : C, 50.1, H, 3.7, Cl, 8.9, Ru, 12.9
Calcd (%) : C, 48.9, H, 3.8, Cl, 9.0, Ru, 12.8

Dicarbonylsulphidedihydridobis (triphenyl phosphine) ruthenium (II): [RuH₂(Pf₃)₂(CS₂)₂]

Benzene solution of [RuCl₂(Pf₃)₄] was suspended into ethanolic aqueous solution of KOH (2N, 10ml) and CS₂ (10ml) and stirred on magnetic stirrer for two hrs at 85°C. On cooling at room temperature yellow coloured crystals were obtained (M. Pt. = 91°C).

Analyses

Found (%) C, 58.6; H, 4.3; Ru, 13.1
Calcd (%) C, 58.5; H, 4.1; Ru, 12.9

Chlorocarbonylcarbodi sulphidehydridobis (Triphenyl Phosphine) ruthenium (II) : [RuHCl(CO)(Pf₃)₂ (CS₂)]

Benzene solution of [RuHCl(CO)(Pf₃)₃] was mixed with 10 ml CS₂ and stirred on magnetic stirrer for one hour and grey coloured crystals were obtained (M.pt=83°C)

Analyses

Found (%) C, 59.7; H, 3.8; Cl, 4.8; Ru, 13.4
Calcd (%) C, 59.6; H, 3.9; Cl, 4.6; Ru, 13.2

Carbon, hydrogen and nitrogen analyses were performed by micro-analysis division RSIC, CDRI, Lucknow. Infrared spectra were recorded in KBr discs on a Perkin-Elmer 621 spectrophotometer and electronic spectra on a Beckmann DU-6 spectrophotometer. Molar conductance (10⁻³m) of complexes were measured in DMF using Wiss-werkstätten weihen obb. type LBR conductivitymeter. Magnetic measurements were made on a gouy balance using Hg[CO(SCN)₄] as calibrant.

RESULTS AND DISCUSSION

All isolated products are air stable coloured solid and soluble in most of the organic solvents and non-electrolyte nature in DMF (10⁻³M). Magnetic moment of all the complexes were found to be diamagnetic suggesting d⁶- configuration of Ru(II). Hence, these complexes have similar octahedral configuration as the parent compound. The ground state of Ru(II) in octahedral crystal field is ¹A_{1g} and two spin allowed transitions ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} may be expected in electronic spectra.

The bands at 500-520 and 460-480 nm in all the complexes are assigned to ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} transitions respectively and octahedral geometry of these complexes may be tentatively assigned. All other transitions in ultra-violet region (290 nm & 336 nm) of very high intensity are assigned CT bands.

The IR spectrum of Pf₃ has been interpreted by Deacon *et al*¹⁵. A close examination of spectra of Pf₃, PPyTH and Ru (II) complexes indicate the following. The VN-H band of PPyTH observed as medium band at 3060 cm⁻¹ shifted to

Table 1: Selected IR bands of ligands and complexes (cm⁻¹)

Compd.	ν Ru-H/ (δ Ru-H)	νCX	Thioamide Bands*			
			I	II	III	IV
PPytTH	(-)	-	1480(s)	1290s 1240m	1090m	785m
[RuH ₂ (CS) ₂ (Pf ₃) (PPytTH)]	2020 (m)	1950 (mb)	1510w 1500w 1490m	1320w 1240m	1040w	760m
[RuHCl(CO)(Pf ₃) (PPytTH) ₂]	2010(m) (740m)	1960(m)	1500w 1490s	1280w 1220w	1050m	770
[RuHCl(CO)(Pf ₃) ₂ (PPytTH)]	2005(m) (720m)	1900(mb)	1520w 1490m 1470m	1050m		760m
[RuH ₂ (CS) ₂ (Pf ₃) ₂]	2030(m)	1335(s)	-	-	-	-
[RuH ₂ (Pf ₃) ₂ (CS ₂) ₂]	2060(m)		-	-	-	-
[RuHCl(CO)(Pf ₃) ₂ (CS ₂)]	2004(m) (710m)	1910(mb)	-	-	-	-
[RuHCl(CS)(Pf ₃) ₃]	2060(m) (720m)	1360(s)	-	-	-	-

* (x=O/ or S)

3300-3240 cm⁻¹ in all complexes as medium broad band. The broadness of the band is probably due to hydrogen bonding of N-H group in the crystal lattice of the solid complexes. Thus, imino nitrogen is intact after coordination to Ru (II) and absence of bonding through imino nitrogen is concluded. The formation of Ru-N bond is ruled out considering the nature of shift and change in intensity of four thioamide bands of PPytTH (Table 1) following previous work¹⁶⁻¹⁹.

All hydrido- complexes display bands at 2010-2060 cm⁻¹ and 710-740 cm⁻¹ assigned to VRu-H and dRu-H respectively²⁰⁻²¹. A medium band at

1900-1950 cm⁻¹ assigned VCO of Co-ordinated carbonyl group²². New bands at 510 and 490 cm⁻¹ also supports these observations and these bands are assigned Vlr-C mode²³. The low position of VC^o O band probably due to trans influence of Pf₃ group.

The coordinated s - bonded²⁴ CS₂ group is indicated by strong bands at 1100-1150 cm⁻¹ and 1510 cm⁻¹.

The new bands of medium intensity at 370-470 cm⁻¹ may be assigned to couple vibrations VRu-Cl+VRu-S/or VRu-P.

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