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

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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 properties 2-4 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 literature11. The precursor complexes [RuCl2(PF3)4]12 and [RuHCl(CO)(PF3)3]]13 were prepared by the method reported in literature.

Suspension of RuCl3 4H2O (0.5g), CS2(10ml), CH3OH (40ml) and NaOH (2N, 15ml) and Triphenyl phosphine (7g) were stirred on magnetic stirror 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 CaCl2.(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): [RuH2(CS)2(PF3)(PPytTH)]

This complex was prepared using [RuH2(CS)2(PF3)2] and PPytTH in molar ratio1:1 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): \([\text{RuHCl(CO)(Pf}_3\text{)(PPytTH)}_2]\)

This deep brown complex was prepared from pink isomer of \([\text{RuH(CO)(Pf}_3\text{)(Cl}_3]\) 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,

Chlorocarbonylhydrodribis(triphenylphosphine) 3-(4'-Pyridyl)-4-phenyl- Triazoline-5-thione ruthenium (II): \([\text{RuHCl(CO)(Pf}_3\text{)(PPytTH)}]\)

This light yellow complex was prepared from yellow isomer of \([\text{RuHCl(CO)(Pf}_3\text{)(Cl}_3]\) 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): \([\text{RuCl}_2(CS}_2\text{)(Pf}_3\text{)(CS}_2]\)

This golden brown complex was prepared starting from Wilkinson compound \([\text{RuCl}_2(Pf}_3\text{)(4)}\) \(^{(12)}\). Benzene solution of \([\text{RuCl}_2(Pf}_3\text{)(4)}\) 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 CaCl\(_2\) (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

Dicarbondisulphidedihydridobis (triphenyl phosphine) ruthenium (II): \([\text{RuH}_2(Pf}_3\text{)(CS}_2]\)

Benzene solution of \([\text{RuH}_2(Pf}_3\text{)(CS}_2]\) was suspended into ethanolic aqueous solution of KOH (2N, 10ml) and CS\(_2\) (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

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 d\(^6\)- 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 \(^1\)A\(_g\) and two spin allowed transitions \(^1\)A\(_g\) \(\rightarrow\) \(^1\)T\(_g\) and \(^1\)A\(_g\) \(\rightarrow\) \(^3\)T\(_g\) may be expected in electronic spectra.

The bands at 500-520 and 460-480 nm in all the complexes are assigned to \(^1\)A\(_g\) \(\rightarrow\) \(^1\)T\(_g\) and \(^1\)A\(_g\) \(\rightarrow\) \(^3\)T\(_g\) 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 Pf\(_3\) has been interpreted by Deacon elal \(^{(15)}\). A close examination of spectra of Pf\(_3\), 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\(^{-1}\))

<table>
<thead>
<tr>
<th>Compd.</th>
<th>v Ru-H/ν(_{\text{CX}}) (δ Ru-H)</th>
<th>Thioamide Bands*</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>PPytTH</td>
<td>(-)</td>
<td>1480s</td>
</tr>
<tr>
<td>[RuH(_2)(CS)(_2)](_2)(PF(<em>3)) (</em>{\text{PPytTH}})</td>
<td>2020(m)</td>
<td>1950(m)</td>
</tr>
<tr>
<td>[RuHCl(CO)(PF(_3))(<em>2)](</em>{\text{PPytTH}})</td>
<td>2010(m)</td>
<td>1960(m)</td>
</tr>
<tr>
<td>[RuHCl(CO)(C(_2)S(<em>2)](</em>{\text{PPytTH}})</td>
<td>2005(m)</td>
<td>1900(mb)</td>
</tr>
<tr>
<td>[RuH(_2)(C(_2)S(_2)](_2)(PF(_3)(_2))</td>
<td>2030(m)</td>
<td>1335(s)</td>
</tr>
<tr>
<td>[RuH(_2)(PF(_3))(_2)(C(_2)S(_2)]</td>
<td>2060(m)</td>
<td>-</td>
</tr>
<tr>
<td>[RuHCl(CO)(PF(_3))(_2)(C(_2)S(_2)]</td>
<td>2004(mb)</td>
<td>1910(mb)</td>
</tr>
<tr>
<td>[RuHCl(CS)(PF(_3))(_3)]</td>
<td>2060(m)</td>
<td>1360(s)</td>
</tr>
</tbody>
</table>

* (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 work\(^{16-19}\).

All hydrido- complexes display bands at 2010-2060 cm\(^{-1}\) and 710-740 cm\(^{-1}\) assigned to VRu-H and dRu-H respectively\(^{20-21}\). A medium band at 1900-1950 cm\(^{-1}\) assigned VCO of Co-ordinated carbonyl group\(^{22}\). New bands at 510 and 490 cm\(^{-1}\) also supports these observations and these bands are assigned VIr-C mode\(^{23}\). The low position of VC\(^{9}\) O band probably due to trans influence of PF\(_3\) group.

The coordinated s-bonded\(^{24}\) CS\(_2\) 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.

REFERENCES


