ijCEPr

International Journal of Chemical, Environmental and Pharmaceutical Research

Vol. 2, No.2-3, 67-71
May-December, 2011

Mixed-ligand Organometallic Derivatives of Rhodium (I) and Iridium (I) with Triphenyl phosphine and 1-Benzoyl-tetrazoline-5-thione

R.N. Pandey*, Kalpana Shahi and D.P. Singh
P.G. Centre of Chemistry (MU), College of commerce, Patna – 800 020 (India)
E-mail : rameshwarnath.pandey@yahoo.com

Article History:
Received: 23 December 2010
Accepted: 23February 2011

ABSTRACT

Four-co-ordinated square planar organometallic derivatives of rhodium (I)and iridium (I) with triphenyl phosphine and 1-benzoyl-tetrazoline-5-thione have been prepared and characterized by elemental, spectroscopic (IR, electronic, ^1H *NMR*), molar conductivity and magnetic susceptibility measurements. The thioamide ligand behaves as neutral monodentale having bonding through thione tautomeric form.

Keywords : Organometallic derivatives, Rh(I), Ir(I), heterocyclic thioamide.

INTRODUCTION

Organometallic derivatives of rhodium[1-3,9] and iridium[8, 27,28] are versatile homogeneous catalyst having unique and interesting insights into structure and bonding. The present study describes synthesis and spectral characterization of some new organometallic derivatives of Wickinson catalyst[12] and Vaska's catalyst[8] with 1-benzoyl tetrazoline-5-thione (BT5TH) (Fig.-1).

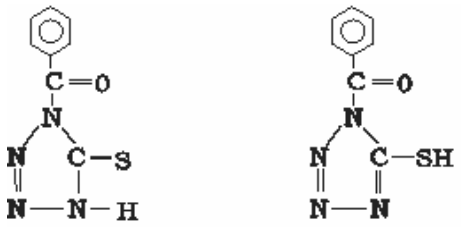

Fig.-1

MATERIALS AND METHODS

All chemicals used were either of Anala R or chemically pure grade. The ligand, 1-benzoyl tetrazoline-5-thione[10], and precursor complenes $[RhX(P\phi_3)_3]$[12], where X= Cl, Br, NCS; $[RhX(CO)(P\phi_3)_2]$[12] , where X= Cl, Br; $[Rh(P\phi_3)_2(CO)(NCS)]$[6] and $[IrCl(CO)(P\phi_3)_2]$[30] were prepared by the method reported in literature. The suspension of freshly prepared precursor complexes in benzene and ethanolic solution of ligand were mixed in desired molar ratios and the solid products were isolated following our earlier method[17].

The products were separated by the addition of the small amount of Absolute ether. The analytical data obtained for the new complexes (Table 1) agree very well with the proposed molecular formulae.
Elemental analyses, magnetic measurement, molecular weight determination, IR, UV-Vis, ^{1}H-NMR spectral data were obtained as we reported earlier [15].

RESULTS AND DISCUSSION

The ligand (BT5TH) contains carbonyl, thiocarbonyl and imino nitrogen atoms as potential donor sites but interacts with thio carbonyl sulphur and acts as monodentate ligand. The softer sulphur atom in the ligand interacts with soft Rh^+ or Ir^+ ions is in agreement with Pearson classifications[18]. On consideration of trans-effect one would anticipate that one of the trans-phosphine groups in $[RhX(CO)(P\phi_3)_2]$ and $[IrCl(CO)(P\phi_3)_2]$ would be labile and undergoes ligand substitution leading to the formation of complexes given in Table 1.

All isolated solid products are diamagnetic indicating the presence of Rh^+ and Ir^+ species. However, oxidation state of rhodium in complexes was further verified by titrating complexes with Ceric ammonium sulphate using ferroin as indicator[11]. The complexes were titrated for two electron charge. The value of molar conductance

of complexes were found to be less than $10\Omega^{-1}cm^2mol^{-1}$ indicating the presence of anions in the inner sphere of complexes and they are of coordinated nature.

Electronic Spectra

Electronic spectra of all rhodium (1) complexes display a very strong broad band between 25000-28000 cm^{-1} assigned to charge transfer. The other ligand field bands are obscured probably due to strong reducing character of Rh^+ species. These observations are in agreement with our earlier work[14] with other thioamide ligands where d-d transition is obscured by charge transfer. However, electronic spectrum of $[RhCl(P\phi_3)(BT5TH)_2]$ exhibits three bands at 13800, 18250 and 23660 cm^{-1}. The first band is broad and weak and may be assigned to spin-forbidden $1A_{1g}\rightarrow 3A_{2g}$ transition. The absorption band at 18250 cm^{-1} may be due to either spin-forbbiden $1A_{1g}\rightarrow 3B_{1g}$ transition or spin-allowed $1A_{1g}\rightarrow 1B_{1g}$ transition[26]. The high value of extinction coefficient suggest it to be the singlet-singlet transition. The band at 23660 cm^{-1} could not be assigned because the ligand (BT5TH) also absorbs in the same region. Thus, all rhodium (1) complexes are iso-structural with precursor complexes (Fig.-2) and are four coordinated.

The two strong bands at 44260 and 27720 cm^{-1} in [Ir Cl(CO)($P\phi_3$)(BT5TH)] assigned to charge transfer and $1A_{1g}\rightarrow 1B_{1g}$ transition in square planar crystal field. The other band at 31240 cm^{-1} is shoulder on CT band supports square planar configuration and assigned to $1A_{1g}\rightarrow 1E_g$ transition. Thus, iridium (1) complex is also iso-structural with precursor complex $[IrCl(CO)(P\phi_3)_2]$ (Fig.-4).

IR Spectra

The infrared spectral bands of interest of the ligand (BT5TH) and complexes are discussed here. A comparison of the IR spectra of BT5TH, $P\phi_3$, Rh (1) and Ir (1) complexes indicate the following :

1. 1-benzoyl tetrazoline-5-thione (BT5TH) contains thioamide group and gives four characteristic bands at 1500 (Band I), 1300 (Band II), 1050 (Band III) and at 820 cm^{-1} (Band IV) due to mixed contributions from $\nu_{C=S}$, $\nu_{C=N}$, δ_{C-H} and δ_{NH} modes[19,24,26]. The red shift of band II, band III and band IV to lower frequencies about 15 cm^{-1}, 30 cm^{-1} and 40 cm^{-1} on complexation to Rh (1) or Ir (1) indicate bonding through thiocarbonyl sulphur[13,16,20].
2. The ν_{N-H} (3220 cm^{-1}) and $\nu_{C=O}$ (1680 cm^{-1}) of free ligand remain present in the spectra of complexes at the same position with undiminished intensity indicating absence of bonding through imino nitrogen and carbonyl group of ligand. This is also supported by blue shift of thioamide band I which has major contribution from δ_{NH} [25].
3. The new bands at 2020, 560 and 510 cm^{-1} in chlorocarbonyl and at 2030, 570 and 500 cm^{-1} in bromo carbonyl complexes of [RhX(CO)($P\phi_3$)(BT5TH)] (X=Cl/Br) are assigned to $\nu_{C\equiv O}$, ν_{asym} Rh-C and ν_{sym} Rh-C modes of coordinated carbonyl group[23]. However, these bands are observed at 1995, 555 and 478 cm^{-1} in [Ir Cl(CO)($P\phi_3$)(BT5TH)].
4. Thiocyanato complexes of rhodium (1) display ν_{CN} at 2110 cm^{-1}, ν_{CS} at 840 cm^{-1} and δ_{NCS} at 485 cm^{-1} is in agreement with diagnostic value assigned by Sabatini el al[2] for terminal NCS group. Turco and Pecile[29] suggested ν_{CS} between 780-860 cm^{-1} for M-N=C=S and at 690-720 cm^{-1} for M-S-C≡N by comparing ν_{CS} of thiocyanato and the corresponding chloro complexes. Thus, Rh-N=C=S bonding may be suggested in the complexes.
5. The presence of single Rh-S stretching band at 330 cm^{-1} in [RhX ($P\phi_3$)($BT5TH)_2$](X=Cl, Br, NCS) indicate two BT5TH molecules are at Trans-disposition in square planar structure (Fig.3).
6. Iridium-chlorine strelehing mode at 305 and 285 cm^{-1} in [Ir Cl(CO)($P\phi_3$)(BT5TH)] complex is in good agreement with Shaw et al[26-28] in view of the trans-influencing nature of CO group. Hence, chlorine is trans to CO and $P\phi_3$ is trans to BTSTH in square planar structure (Fig.-4).

^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the free 1-benzoyl tetrazoline-5-thione and their metal complexes were recorded in $CDCl_3$/TMS to substantiate further metal-ligand bonding. The spectra of complexes display multiplates in the region $\delta_{6.64-7.32}$ PPM due to aromatic proton of coordinated $P\phi_3$ molecule[7]. However, the phenyl protons of 1-benzoyl tetrazoline-5-thione appears in the region $\delta_{7.42-7.76}$ PPM on complexation. The peak is broad

and may be due to the presence of four nitrogen atoms which display large quadrupole resonance broadening effect[30] or carbonyl oxygen of the ligand. The imino group proton signal is masked by the strong and broad signal of phenyl protons. This is indicated by the relative area of phenyl proton peak which is greater by two units than required for phenyl protons. Thus, the N-H group of ligand is intact on complexation and coordination occurs through thiocarbonyl sulphur. These observations are consistent with conclusion drawn from IR spectral studies.

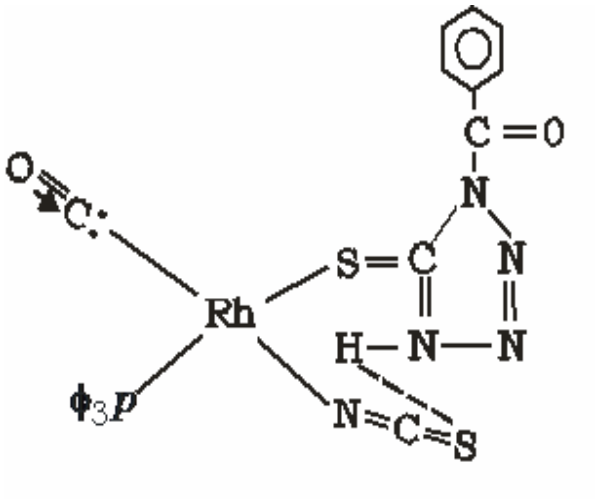

Fig.-2

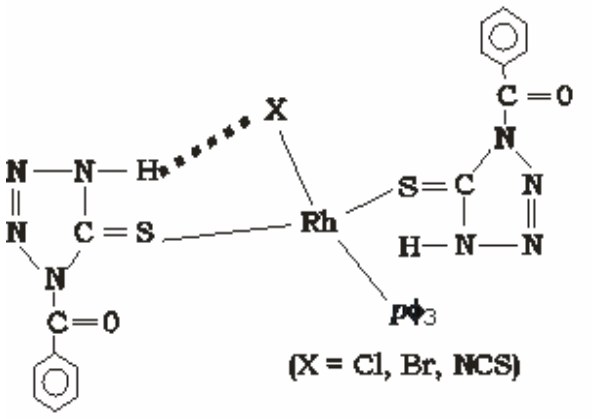

Fig.-3

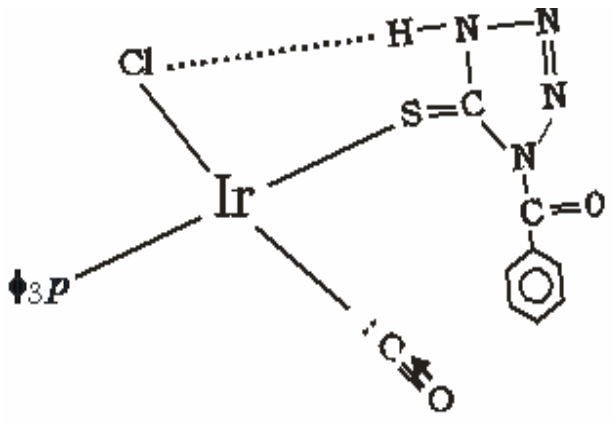

Fig.-4

Table 1 : Analytical and Electronic spectral data of complexes

Complex/(Colour)	Analysis % Found/(Calcd)				$\lambda_{max}(cm^{-1})$/ (Assignment)
Exp. Formula	C	H	N	Metal Rh	
$[Rh\ Cl\ (P\phi_3)\ (BT5TH)_2]$ (light brown) $C_{32}H_{27}O_2N_8PS_2Cl\ Rh$	50.32 (50.21)	3.32 (3.35)	14.01 (13.78)	12.80 (12.67)	42000 (CT Band) 23670 $(T_{2g} \rightarrow \pi^*)$ 18160 $(1A_{1g} \rightarrow 1B_{1g})$ 13785 $(1A_{1g} \rightarrow 3A_{2g})$
$[Rh\ Br\ (P\phi_3)(BT5TH)_2]$ (Brown) $C_{32}H_{27}O_2N_8PS_2Br\ Rh$	47.82 (47.60)	3.22 (3.15)	13.11 (13.06)	12.23 (12.01)	43480 (CT Band) 29240 $(T_{2g} \rightarrow \pi^*)$
$[Rh(NCS)(P\phi_3)(BT5TH)_2]$ (yellow) $C_{33}H_{27}N_9O_2S_3P \cdot Rh$	50.32 (50.29)	3.33 (3.23)	15.21 (15.08)	12.35 (12.33)	41660 (CT Band) 28185 $(T_{2g} \rightarrow \pi^*)$
$[Rh\ Cl\ (CO)\ (P\phi_3)(BT5TH)]$ (Yellowish Brown) $C_{26}H_{21}N_4O_2SP\ Cl\ Rh$	51.31 (51.22)	3.30 (3.32)	8.68 (8.85)	16.23 (16.28)	37740 (CT Band) 29420 $(T_{2g} \rightarrow \pi^*)$
$[Rh\ Br\ (CO)\ (P\phi_3)(BT5TH)]$ (Brown) $C_{26}H_{21}N_4O_2SP\ Br\ Rh$	47.90 (47.85)	3.12 (3.10)	8.35 (8.27)	15.40 (15.21)	37740 (CT Band) 29420 $(T_{2g} \rightarrow \pi^*)$
$[Ir\ Cl\ (CO)\ (P\phi_3)\ (BT5TH)]$ (Brown) $C_{26}H_{21}N_4O_2SP\ Cl\ Ir$	43.63 (43.83)	3.00 (2.95)	7.92 (7.86)	27.02 (27.00)	44260 (CT Band) 38162 $(1A_{1g} \rightarrow 1B_{1g})$ 31240 $(1A_{1g} \rightarrow 1E_g)$

REFERENCES

1. Barros H.J.V., Ospina M.L., Arguello E., Rocha W.R., Gusevskaya E. and Santos E.N. dos.; J. Organomet. Chem. **671** (2003), 150.
2. Bertini I. and Sabatini A., Inorg. Chem., **5** (1966), 837.
3. Da Silva A.C., Oliveira K.C.B., Gusevskaya E.V. and dos. Sautos E.N., J. Mol. Catal. (A), **179** (2002), 133.
4. Greaves E.O., Lock C.J.L. and Maitls, Can J. Chem., **46**, (1968) 3879.
5. Jenkins J.M. and Shaw B.L., J. Chem. Soc., **1407** (1965), 6789.
6. Jennings M.A. and Wojcicki A., Inorg. Chem., **6** (1967) 1854.
7. Kanchanadevi S., Balasubramanian K.P., Chinnusamy V., Karvembu R. and Natarajan K., Trans. Met. Chem., **30**, (2005) 330.
8. Kon Kol M. and Steinborn D., J. Organomet. Chem., **691** (2006), 2839.
9. Landaeta Vanessa R., Peruzzini Maurizio, Herrera Veronica, Bianchini Claudio, Sanchez-Delgado Roberto A., Goeta Andres E. and Zanobini Fabrizio, J. Organomet. Chem., **691**(2006), 1039.
10. Lieber E. and Ramchandran J., Can. J. Chem., **37** (1959), 101.
11. Martin B., McWhinnie W.R. and Waind G.M., J. Inorg. Nucl. Chem., **23** (1961), 207.
12. Osborn J.A., Jardine F.H., Young J.F. and Wilkinson G., J. Chem. Soc., **A**, 1711 (1966).

13. Pandey R.N., Kumar Ashok and Singh D.P., Asian J. Chem., **22(3)** (2010), 1661.
14. Pandey R.N. and Singh Rajnish Kr., J. Ultra Sc., **21(3)** (2009), 579.
15. Pandey R.N. and Kumar Ashok, Oriental J. Chem., **24** (2008), 697.
16. Pandey R.N. and Das J.N., J. Indian Chem. Soc., **71** (1994), 187.
17. Pandey R.N., Kumar Arun, Singh R.S.P., Sahay A.N. and Kumar Shashikant, J. Indian Chem. Soc., **69** (1992), 804.
18. Pearson R.G., Chem. Ber., **3** (1967), 103.
19. Rao C.N.R. and Venkataraghavan R., Can. J. Chem., **42** (1964), 43.
20. Sharma R.N., Giri Poonam, Kumar Amritesh, Kumari Alpna and Pandey R.N., J. Indian Chem. Soc., **83** (2006), 1139.
21. Shaw B.L. and Deeming A.J., J. Chem. Soc., **A**(1969) 1128.
22. Shaw B.L. and Smithies A.C., J. Chem. Soc., **A**(1967) 1047.
23. Singh M.M. and Dutta Dipak K., J. Indian Chem. Soc. Dutta, **70** (1993), 59.
24. Singh B., Sinha R.J., Pandey R.N. Tiwari H.N. and Bhanu Uday, J. Indian Chem. Soc., **60** (1983), 415.
25. Singh B., Singh R., Choudhari R.V. and Thakur K.P., Indian J. Chem., **11** (1973), 174.
26. Singh B. and Agarwala U., J. Inorg. Nucl. Chem., **33** (1971), 598.
27. Tang W. and Zhang X., Chem. Rev. **103** (2003), 3029.
28. Terry T., Au-yeung L. and Chan A.S.C., Coord. Chem. Rev. **248** (2004), 2151.
29. Turco A. and Pecile C., Nature, **191** (1961), 66.
30. Vaska L. and Di Luzio J.W., J. Am. Chem. Soc. ,**83** (1961), 2784.

[IJCEPR-137/2010]