



Synthesis, Characterization and Reactivity Studies on Mixed-Ligand Organometallic Complexes of Rhodium and Iridium with Triphenyl phosphine and Ethylene thiourea

R.N. PANDEY*, KALPANA SHAHI and PREETY PANDEY

P.G. Centre of Chemistry, College of Commerce, Patna-800 020, India

*Corresponding author: E-mail: rameshwarnath.pandey@yahoo.com

(Received: 24 August 2011;

Accepted: 9 May 2012)

AJC-11464

Mixed ligand organometallic complexes of rhodium and iridium with triphenyl phosphine and ethylene thiourea have been prepared and characterized by chemical, spectroscopic (IR and electronic), molar conductivity and magnetic susceptibility measurements. Rhodium(I) complexes were iso-structural with precursors and are four co-ordinated square planar; iridium(I) complexes show square planar structure whereas iridium(III) complexes exhibit octahedral structure. The thioamide ligand behaves as neutral monodentate having bonding through thione tautomeric form.

Key Words: Organometallic derivatives, Rh(I), Ir(I), Ir(III), Heterocyclic thioamide.

INTRODUCTION

Organometallic complexes of rhodium¹⁻³ and iridium⁴⁻⁷ are versatile catalyst for many organic reactions. They have unique and interesting insight into structure, bonding and reactivity of molecules. A literature survey revealed that less amount of work have been done with mixed thioamide ligand. In continuation of our earlier work⁸⁻¹³, we report synthesis, characterization and reactivity of some new mixed ligand organometallic complexes of rhodium and iridium using ethylene thiourea as thioamide ligand.

EXPERIMENTAL

All chemicals used were of AnalR or chemically pure grade. The ligand (etu)¹⁴ and precursor complexes, [RhCl(Pφ₃)₂(etu)]¹¹, [RhX(CO)(Pφ₃)₂(etu)]¹³ (X = Cl, Br) and [IrCl(CO)(Pφ₃)₂(etu)]¹¹ were prepared as our earlier method reported in literature.

Preparation of complexes

Preparation of [Rh(Pφ₃)₂(etu)(Py)]X (X = BF₄/PF₆): A solution of [RhCl(Pφ₃)₂(etu)] (0.910 mg) in methanol (20 mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (7.58 mmol) in methanol (10 mL) for 1 h to afford an orange solution. A solution of NH₄BF₄/NH₄PF₆ (1 mmol) in methanol (5 mL) was added to previous solution. The mixture was further concentrated to half of original volume and 15 mL dry ether was added. The light orange coloured solid separated which after filtration was washed with methanol, ether and dried in vacuum yield 85 %.

1. [Rh(Pφ₃)₂(Py)etu]BF₄: Calculated for RhC₄₄H₄₁N₃P₂SBF₄: (% C, 59.00; H, 4.58; N, 4.69; Rh, 11.51 %; Found (%): C, 58.96; H, 4.56; N, 5.01; Rh, 11.50;

2. [Rh(Pφ₃)₂(etu)(Py)]PF₆: Calculated for RhC₄₄H₄₁N₃P₃SF₆: H, 4.30; N, 4.40; Rh, 10.80; Found (%): C, 55.55; H, 4.31; N, 4.42; Rh, 10.85.

Preparation of [RhX(Pφ₃)(CO)(etu)] (X = Cl/Br): The suspension of freshly prepared precursor complexes [RhX(CO)(Pφ₃)₂]¹⁵ (X = Cl/Br) in benzene (10 mL) and methanolic solution of ethylene thiourea (etu) in equimolar ratio was stirred on magnetic stirrer at 85 °C for 1 h. The working mixture was concentrated to 5 mL and ether was added to the cold solution and the solid precipitate was washed with ether and dried over anhydrous CaCl₂.

3. [RhCl(Pφ₃)(CO)(etu): Calculated (%) for RhC₂₂H₂₁N₂SPOCl: C, 49.76; H, 3.95; N, 5.27; Rh, 19.41; Found (%) : C, 50.10; H, 3.89; N, 5.21; Rh, 19.20.

4. RhBr(Pφ₃)(CO)(etu): Calculated (%) for RhC₂₂H₂₁N₂SPOBr: C, 45.91; H, 3.65; N, 4.86; Rh, 17.91; Found (%): C, 46.01; H, 3.62; N, 4.45; Rh, 18.21.

Preparation of [Ir(CO)(Pφ₃)(etu)(Py)]X (X = BF₄/PF₆): A suspension of [Ir(CO)(Pφ₃)(etu)Cl] in methanol (20 mL) was stirred on magnetic stirrer until the solid dissolved completely and treated with an excess of pyridine (7.58 mmol) in methanol (8 mL) for 1 h. A solution of NH₄PF₆ or NH₄BF₄ or in methanol (5 mL) was added and concentrated under vacuum. The orange solid separated was filtered, washed with methanol and finally dried under vacuum over anhydrous CaCl₂.

5. $[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{etu})(\text{Py})]\text{PF}_6$: Calculated (%) for $\text{IrC}_{27}\text{H}_{26}\text{N}_3\text{OSP}_2\text{F}_6$: C, 40.09; H, 3.21; N, 5.19; Ir, 23.76; Found (%): C, 40.21; H, 3.22; N, 5.20; Ir, 23.81.

6. $[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{etu})(\text{Py})]\text{BF}_4$: Calculated (%) for $\text{IrC}_{27}\text{H}_{26}\text{N}_3\text{OSPBF}_4$: C, 43.21; H, 3.46; N, 5.60; Ir, 25.60; Found (%): C, 43.26; H, 3.45; N, 5.66; Ir, 25.86.

Preparation of $[\text{IrXPh}(\text{CO})(\text{P}\phi_3)_2(\text{etu})]\text{BF}_4$ (X = Cl/Br):

To refluxing solution of $[\text{IrX}(\text{CO})(\text{P}\phi_3)_2]$ (X = Cl/Br) (1 mmol) in benzene (10 mL) and ethylene thiourea (1 mmol) in methanol (15 mL), $\text{PhN}_2^+\text{BF}_4^-$ (0.025 g) in acetone (5 mL) was added and bright orange solution changes to pale yellow after 2 h. The pale yellow solution was concentrated to half volume and ether added to the cold solution. A white colour solid separated out. It was filtered, washed with ether and dried in vacuum over anhydrous CaCl_2 .

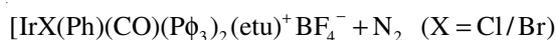
7. $[\text{IrCl}(\text{Ph})(\text{CO})(\text{P}\phi_3)_2(\text{etu})]\text{BF}_4$: Calculated (%) for $\text{IrC}_{46}\text{H}_{41}\text{N}_2\text{OP}_2\text{SCl}\cdot\text{BF}_4$: C, 52.80, H, 3.92; N, 2.67; Ir, 18.36; Found (%): C, 52.90; H, 4.01; N, 2.82; Ir, 18.50;

8. $[\text{IrBr}(\text{Ph})(\text{CO})(\text{P}\phi_3)_2(\text{etu})]\text{BF}_4$: Calculated (%) for $\text{IrC}_{46}\text{H}_{41}\text{N}_2\text{OP}_2\text{SBr}\cdot\text{BF}_4$: C, 50.65; H, 3.76; N, 2.56; Ir, 17.61; Found (%): C, 50.70; H, 3.78; N, 2.55, Ir, 17.90.

Elemental analysis was performed by the micro analytical section RSIC, CDRI, Lucknow. Infrared spectra of ligand and complexes were recorded on a Perkin-Elmer 577 spectrophotometer in the range of $4000\text{--}200\text{ cm}^{-1}$ as KBr pellets and electronic spectra on a Beckmann DU 6 spectrophotometer. The molar conductance (10^{-3} M) of complexes were measured in DMF using Wiss-Wekstatter Weithem obb type LBR conductivity meter. The magnetic measurements were made on a gouy balance.

RESULTS AND DISCUSSION

All organometallic complexes formed were stable solid at atmospheric conditions and fairly soluble in DMF and DMSO. Analytical results were satisfactory and support proposed stoichiometry. Sigma-aryl complexes of iridium(III) were formed by oxidative addition of phenyl ion to iridium(I) complexes $[\text{IrX}(\text{CO})(\text{P}\phi_3)_2]$ (X = Cl/Br) in presence of ethylene thiourea.



Removal of chloride ligand from the precursor complex $[\text{IrCl}(\text{CO})(\text{P}\phi_3)(\text{etu})]$ were readily achieved by ligand substi-

tution using excess of a strong σ -donor such as pyridine in the presence of NH_4PF_6 or NH_4BF_4 (S. No. 5 and 6). The molar conductance value in DMF (10^{-3} M) were in agreement with required by 1:1 electrolytes (S.No. 1, 2, 5, 6, 7 and 8) which was further confirmed by IR spectra. All rhodium(I) complexes were diamagnetic indicating univalent rhodium (Rh^+). However, oxidation state of metal in complexes were verified by titrating the complexes with ceric ammonium sulphate using ferroin as indicator¹⁶. The complexes were titrated for two electron charge. Electronic spectra of complexes display a very broad band of strong intensity between $24600\text{--}24000\text{ cm}^{-1}$ assigned to charge transfer band ($\text{T}_{2g} \rightarrow \pi^*$). The other ligand field bands are obscured due to strong reducing character of Rh^+ species. These observations are in agreement with our previous work¹⁵ observed for other thioamide ligands and previous literature¹⁷. Thus, rhodium(I) complexes are iso-structural with precursors and are four-coordinated square planar¹⁵.

Electronic spectra of iridium(I) complexes (S. No. 5 and 6) display a very strong band of considerable high intensity at $39215\text{--}38460\text{ cm}^{-1}$ probably due to charge transfer. Considering diamagnetic nature and known preferential square planar structure of all iridium(I) complexes was assumed and all are iso-structural to precursor complex $[\text{IrCl}(\text{CO})(\text{P}\phi_3)(\text{etu})]$. The σ -aryl complexes of iridium(III) (S. No. 7 and 8) exhibits strong intensity band at 30770 cm^{-1} due to charge transfer. Two spin-allowed transitions at 25100 cm^{-1} and 29310 cm^{-1} are consistent with octahedral structure¹¹ and assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions respectively. One spin-forbidden transition band at 24210 cm^{-1} was also present and assigned to $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ transition.

IR spectra: The spectrum of $\text{P}\phi_3$ is recorded and interpreted by Deacon *et al.*¹⁸ and etu molecule by Meek and Co-workers¹⁹. Agarwala and Rao²⁰ have performed the normal coordinate analysis (NCA) of etu molecule. A comparison of the spectra of $\text{P}\phi_3$, etu and corresponding complexes indicate the formation of metal-P and metal-S bonding. The formation of metal-S bonding results in a decrease in the frequency of thioamide band IV by $20\text{--}25\text{ cm}^{-1}$ consistent with our earlier report²¹. The systematic change in position and intensity of other thioamide bands (Table-1) also supports the formation of metal-S bond and good agreement with previous literature²²⁻²⁴. The $\nu(\text{NH})$ band of etu remains almost unchanged in position or blue shift to higher frequency indicating absence of bonding through imino nitrogen.

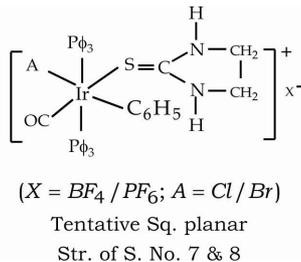
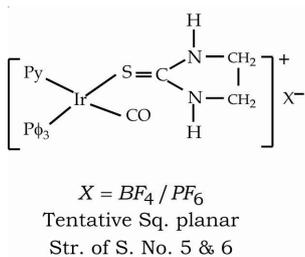
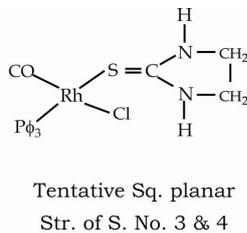
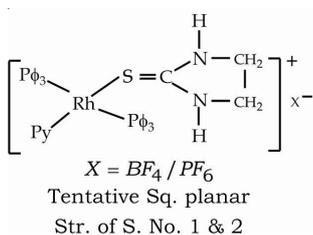
TABLE-1

Compound	Thioamide bands*				$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{S})$
	Band I	Band II	Band III	Band IV		
Ligand (etu)	1530 (s)	1200 (s)	1040 (m)	685 (s)	–	–
$[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{etu})]\text{BF}_4$	1530 (s)	1190 (s)	1030 (m)	660 (m)	–	380 (w), 260 (w)
$[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{etu})]\text{PF}_6$	1535 (s)	1190 (m)	1025 (m)	665 (m)	–	410 (w), 310 (w)
$[\text{RhCl}(\text{CO})(\text{P}\phi_3)(\text{etu})]$	1532 (s)	1185 (m)	1020 (m)	660 (m)	2027 (m)	425 (w), 310 (w)
$[\text{RhBr}(\text{CO})(\text{P}\phi_3)(\text{etu})]$	1535 (s)	1180 (m)	1020 (m)	655 (m)	2020 (m)	420 (w)
$[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{Py})(\text{etu})]\text{PF}_6$	1535 (s)	1178 (m)	1020 (m)	660 (m)	2040 (m)	420 (w), 310 (w)
$[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{Py})(\text{etu})]\text{BF}_4$	1530 (s)	1170 (m)	1010 (m)	660 (m)	2045 (m)	430 (w), 310 (w)
$[\text{IrCl}(\text{Ph})(\text{CO})(\text{P}\phi_3)_2(\text{etu})]\text{BF}_4$	1530 (s)	1180 (m)	1005 (m)	660 (m)	2040 (m)	425 (w), 315 (w)
$[\text{IrBr}(\text{Ph})(\text{CO})(\text{P}\phi_3)_2(\text{etu})]\text{BF}_4$	1530 (s)	1175 (m)	1000 (m)	662 (m)	2050 (m)	430 (w), 320 (w)

*Band I: [60 % $\delta_{\text{sym}}(\text{NH})$ + 20 % $\nu_{\text{sym}}(\text{C}-\text{N})$]; Band II: [30 % $\nu_{\text{sym}}(\text{C}-\text{N})$ + 36 % $\nu(\text{C}=\text{S})$ + 24 % $\delta_{\text{sym}}(\text{NH})$]; Band III: [34 % (CH_2-N) + 34 % $\nu(\text{C}-\text{C})$ + 26 % $\nu(\text{C}=\text{S})$]; Band IV: [46 % $\nu(\text{C}-\text{N})$ + 30 % $\nu(\text{C}=\text{S})$ + 11 % asym. ring deformation].

All the characteristic bands of $P\phi_3$, CO (carbonyl) and pyridine have been observed in the spectra of complexes^{10,25,26}.

New bands at 315, 270 and 250 cm^{-1} in the spectra of σ -aryl complexes (S. No. 7) could be assigned as Cl-Ir-Ph in view of the *trans*-influencing nature of σ -bonded aryls²⁷. The presence of single $\nu(\text{Ir-P})$ (385-380 cm^{-1}) stretching mode in complexes (S. No. 7 and 8) indicate two $P\phi_3$ molecules are at *trans*-disposition in octahedral structure. The compound S. No. 3 exhibit multiple $\nu(\text{Rh-Cl})$ absorptions in the 260-350 cm^{-1} region and absent in bromo complex (S. No. 4). The characteristic bands due to counter anions were observed at 1105 cm^{-1} for BF_4^- and 1070 cm^{-1} for PF_6^- in the spectra of respective complexes. These bands are not present in other complexes (S. No. 3 and 4). Thus, tentative structure of all new complexes may be proposed as:



2. H.J.V. Barros, M.L. Ospina, E. Arguello, W.R. Rocha, E. Gusevskaya and E.N. dos Santos, *J. Organomet. Chem.*, **671**, 150 (2003).
3. J.A. Osborn, F.H. Jardine and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
4. E. Farnetti and N.Z. Marsich, *J. Organomet. Chem.*, **689**, 14 (2004).
5. J.M. O'Connor, A. Closson, K. Hiibner, R. Merwin and P. Gantzel, *Organometallics*, **20**, 3710 (2001).
6. S. Saito and Y. Yamamoto, *Chem. Rev.*, **100**, 2901 (2000).
7. D. Benito-Garagorri and K. Kirchner, *Acc. Chem. Res.*, **41**, 201 (2008).
8. R.N. Pandey, A. Kumar, R.S.P. Singh, A.N. Sahay and S. Kumar, *J. Indian Chem. Soc.*, **69**, 804 (1992).
9. R.N. Pandey, S. Kumar, S. Kumar, R.R. Choudhary and A.N. Sahay, *Indian J. Chem.*, **32A**, 987 (1993).
10. R.N. Pandey and A.K. Nag, *Rasayan J. Chem.*, **4**, 142 (2011).
11. R.N. Pandey, G. Kumari, A. Kumar and R.K. Singh, *Int. J. Chem. Sci.*, **8**, 951 (2010).
12. R.N. Pandey and J.N. Das, *J. Indian. Chem. Soc.*, **71**, 187 (1994).
13. R.N. Pandey, D.P. Singh, Priya and R.K. Singh, *Orient. J. Chem.*, **26**, 1513 (2010).
14. A.J. Van, Organic Synthesis Collections, John Wiley & Sons, New York, Vol. III, p. 394 (1955).
15. R.N. Pandey and R.K. Singh, *J. Ultra Scient. Phys. Sci.*, **21**, 579 (2009).
16. B. Martin, W.R. Mcwhinnie and G.M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).
17. T. Ramasami and J.E. Espenson, *Inorg. Chem.*, **19**, 1523 (1980).
18. G.B. Deacon and J.H.S. Green, *Spectrochim. Acta A*, **24**, 845 (1968).
19. R. Meck and A. Luttringhaus, *Chem. Ber.*, **90**, 975 (1957).
20. U. Agarwala and P.B. Rao, *Indian J. Pure Appl. Phys.*, **7**, 299 (1989).
21. R.N. Pandey, S. Kumar, S. Kumar and S.K. Singh, *Asian J. Chem.*, **6**, 460 (1994).
22. B. Singh, R. Singh, R.V. Choudhary and K.P. Thakur, *Indian J. Chem.*, **11**, 174 (1973).
23. C.N.R. Rao, R. Venkataraghavan and T.R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
24. R.N. Pandey, G. Kumari and R.K. Singh, *Orient. J. Chem.*, **25**, 625 (2009).
25. R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
26. E. Sola, J. Navarro, J.A. Lopez, F.J. Lahoz, L.A. Oro and H. Werner, *Organometallics*, **18**, 3534 (1999).
27. N. Farrell and D. Sutton, *Can. J. Chem.*, **55**, 360 (1977).

REFERENCES

1. A.C. da Silva, K.C.B. de Oliveira, E.V. Gusevskaya and E.N. dos Santos, *J. Mol. Catal. A*, **179**, 133 (2002).