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Organoruthenium (II) Complexes with Thioamide Ligands

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(Received: January 09, 2011; Accepted: February 12, 2011)

ABSTRACT

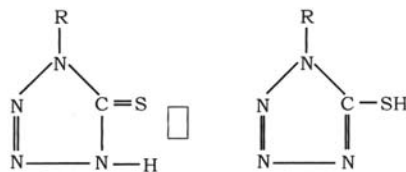
Some new mixed ligand phosphine and arsine complexes of organoruthenium (II) with substituted 1, 2, 4-tetrazoles have been synthesized and characterized using elemental analysis, conductivity, magnetic, electronic, IR, ^1H NMR and ^{31}P NMR spectral measurements. IR spectral data provide un-ambiguous evidence for coordination through nitrogen (Ru-N) and sulphur (Ru-S) of the ligand and acts as mononegative bidentate. ^{31}P NMR spectra of complexes confirmed the magnetically equivalent phosphorous atoms suggesting two po_3 groups trans to each other in octahedral structure.

Key words: Organoruthenium (II), Mixed-ligand triphenyl phosphine, triphenyl arsine, Thioamides.

INTRODUCTION

Organometallic Chemistry of ruthenium (II) is currently receiving a lot of attention due to catalytic¹⁻³ medicinal⁴⁻⁵, anti-bacterial⁶ and significant biological activities⁷⁻⁸. The present communication comprises synthesis, spectral characterization structural investigations and nature of metal ligand

bonding in some new organometallic compounds of ruthenium (II) with 1, 2, 3, 4 – tetrazoles having thioamide group (I). Moreover, the ligands selected for study are claimed to possess anti-convulsant⁹, radio protective¹⁰ and spermatostatic¹¹ properties. The anti-bacterial activities against staphylococcus aureus and Escherichia Coli have been reported by copwer *et al.*,¹².



(I)

(R = -C₄H₉; -CH₂C₆H₅; -2, 6 (CH₃)₂C₆H₃)

EXPERIMENTAL

All the reagent used were of anal R or chemically pure grade. Solvents were dried before use. 1-substituted tetrazoline-s-thione were prepared by the method described by Lieber *et al.*¹³ The precursor complexes [Ru HCl (CO) (p ϕ_3)₃]¹⁴ and [Ru HCl (CO) As ϕ_3)₃]¹⁵ were prepared according to the literature procedures.

Procedure

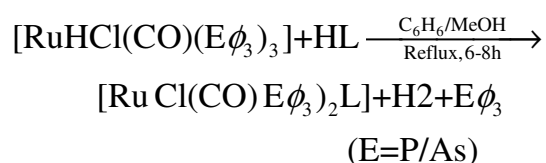
Preparation of Complexes

To a solution of [Ru HCl (CO) (p ϕ_3)₃] (950 mg, 1 m-mol) Or [Ru HCl (CO) As ϕ_3)₃] (1 g, 1m.mol) in benzene (30 ml) the respective ligands (1m.mol) were added. The resulting solution was stirred on magnetic stirrer and concentrated to Ca. 5 ml and the product was separated by the addition of ether. It was filtered and dried in vacuum (yield = 75.80%).

The C, H and N analyses were performed at the C.D.R.I, Lucknow, India. ¹H and ³¹P NMR spectra were recorded on Bruker 400 MHz or varian F x 90Q instruments using TMS and orthophosphoric acid as references, respectively. Electronic spectra were recorded with Zeiss (Jena) model of automatic recording system. IR spectra of ligands and complexes were recorded by means of Perkin-Elmer 521 spectrophotometer in the range of 4000 – 200 cm⁻¹ using KBr pellets. Molar conductance of complexes were measured in DMF using Wiss-Werkstatter Weithem obb type conductivity meter. The magnetic moment of the complexes were measured at 300 K using gouy balance.

RESULTS AND DISCUSSION

All thioamide ligands interacts with precursor complexes in a 1 : 1 molar ratio in giving solid derivatives [Ru HCl (CO) (E ϕ_3)₃L] (E = P/As; HL = ligands) and acts as mononegative bidentate ligands.



Complexes are thermally stable up to 150°C, non-hygroscopic, air-stable and shiny crystalline solids. These are sparingly soluble in methanol, benzene, soluble in dichloromethane, acetone, acetonitrile, DMF, DMSO and insoluble in diethyl ether. Analytical data of the complexes are consistent with our formulations. The conductance behavior suggest their non-electrolytic nature.

Electronic Spectra

All complexes are diamagnetic indicating the presence divalent ruthenium (d⁶) and 1A_{1g} ground term in octa hedral crystal field. Two spin allowed transitions 1A_{1g} → 1T_{1g} and 1A_{1g} → 1T_{2g} may be expected¹⁶. The electronic spectral bands at 20400 – 19230 cm⁻¹ and 18660 – 16600 cm⁻¹ assigned to 1A_{1g} → 1T_{1g} and 1A_{1g} → 1T_{2g} transition respectively indicate octahedral structure of complexes¹⁷. The other high intensity bands in UV region at 28570 cm⁻¹ (T_{2g} → π*) and at 34480 cm⁻¹ are probably due to charge transfer. The nature of the electronic spectra are similar to those observed for other octahedral ruthenium (II) complexes¹⁸.

IR Spectra

A comparison of IR spectra of ligands and respective complexes indicate formation of Ru-S and Ru-N bonds. The ν_{S-H} (2550 cm⁻¹) and ν_{NH} (3180 cm⁻¹) bands of ligand disappear from the spectra of complexes indicating deprotonation of imino proton on complexation and formation of Ru – N bond. The formation of simultaneous Ru – S and Ru – N bond blue shift thioamide band II (20-30 cm⁻¹) and red shift thioamide band I (15-20 cm⁻¹), band III (25-30 cm⁻¹) and band IV (30-40 cm⁻¹) of ligand due to increase in CN bond order and decrease in CS bond order.¹⁹⁻²¹ The terminal coordinated C≡O group appeared at 1944-1980 cm⁻¹ in all complexes and the characteristic bands due to P ϕ_3 or AS ϕ_3 are also present in the expected region²².

¹H NMR and ³¹P NMR spectra

All the complexes showed signals in the δ8.20- 8.99 PPM range due to the aromatic protons of p ϕ_3 /As ϕ_3 ²³. However, broad multiplet in the δ7.5-8.0 PPM region due to phenyl protons of ligands. The broadening of this peak probably due to presence of four nitrogen atoms which may cause large quadrupole resonance broadening effect. The

Table 1: Analytical data of new Ru(II) complexes

Complex/(Colour)	Analysis (%) : Found (Calcd)				λ_{max} (Cm ⁻¹)	Assignment
	C	H	N	Ru		
Molecular formula	59.38	4.60	6.61	11.95	19230	(¹ A _{1g} → ¹ T _{1g})
[RuCl(CO)(P ₃) ₂ L]	(59.60)	(4.61)	(6.62)	(11.94)	16660	(¹ A _{1g} → ¹ T _{2g})
(yellow)					28570	(T _{2g} → π^*)
RuC ₄₂ H ₃₉ N ₄ OP ₂ SCI					34480	(CT intra ligand)
[RuCl(CO)(As ₃) ₂ L ₁]	53.90	4.10	6.11	10.90	19600	(¹ A _{1g} → ¹ T _{1g})
(dull yellow)	(53.99)	(4.17)	(5.99)	(10.81)	16950	(¹ A _{1g} → ¹ T _{2g})
RuC ₄₂ H ₃₉ N ₄ OAs ₂ SCI					28735	(T _{2g} → π^*)
					35715	(π - π^* intra-ligand)
[RuCl(CO)(P ₃) ₂ L ₁]	61.30	4.10	6.51	11.50	19230	(¹ A _{1g} → ¹ T _{1g})
(yellow)	(61.32)	(4.20)	(6.36)	(11.48)	16950	(¹ A _{1g} → ¹ T _{2g})
RuC ₄₅ H ₃₇ N ₄ OP ₂ SCI					28575	(T _{2g} → π^*)
					35090	(CT intra-ligand)
[RuCl(CO)(As ₃) ₂ L ₁]	55.92	3.79	5.79	10.40	19420	(¹ A _{1g} → ¹ T _{1g})
(faint yellow)					16950	(¹ A _{1g} → ¹ T _{2g})
RuC ₄₅ H ₃₇ N ₄ OAs ₂ SCI	(55.81)	(3.82)	(5.78)	(10.43)	33890	(T _{2g} → π^*)
					34245	(CT Intra-ligands)
[RuCl(CO)(P ₃) ₂ L ₂]	61.68	4.40	6.28	11.35	19450	(¹ A _{1g} → ¹ T _{1g})
(yellow)	(61.77)	(4.36)	(6.26)	(11.30)	16720	(¹ A _{1g} → ¹ T _{2g})
RuC ₄₆ H ₃₉ N ₄ OP ₂ SCI					28570	(T _{2g} → π^*)
					35090	(CT Band Intra-ligands)
[RuCl(CO)(As ₃) ₂ L ₂]	56.31	3.95	5.75	10.30	19270	(¹ A _{1g} → ¹ T _{1g})
(Dull yellow)	(56.24)	(3.97)	(5.70)	(10.29)	16530	(¹ A _{1g} → ¹ T _{2g})
RuC ₄₆ H ₃₉ N ₄ OAs ₂ SCI					28400	(T _{2g} → π^*)
					35090	(CT Band)

LH = C₅H₁₀N₄S; L₁H = C₈H₈N₄S; L₂H = C₉H₁₀N₄S

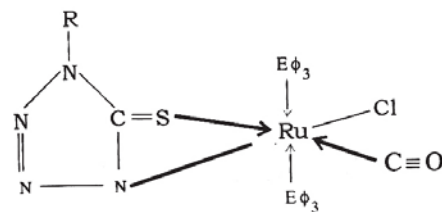
Table 2: IR, ¹H NMR and ³¹P NMR spectral data

Compd.	Thio amide Bands (cm ⁻¹)				¹ H NMR (PPM)			³¹ P NMR (PPM)
	I	II	III	IV	Aromatic Protons	N-H Protons	CH ₃ Protons	
HL (ligand)	1500s	1280m	1065m	805m	-	1.52	2.93	-
[RuCl(CO)(P ₃) ₂ L]	1485s	1305m	1045m	770m	7.92	-	2.92	28.72
[RuCl(CO)(As ₃) ₂ L]	1480s	1300m	1050m	775m	8.00	-	2.94	-
HL ₁ (ligand)	1510s	1290m	1050m	810m	7.85	1.54	-	-
[RuCl(CO)(P ₃) ₂ L ₁]	1490s	1310m	1030m	765m	7.86	-	2.93	28.82
[RuCl(CO)(As ₃) ₂ L ₁]	1500s	1315m	1035m	780m	7.92	-	2.95	-
HL ₂ (ligand)	1504s	1286m	1055m	790m	7.56	1.51	2.95	-
[RuCl(CO)(P ₃) ₂ L ₂]	1495s	1305m	1045m	765m	7.86	-	2.98	28.80
[RuCl(CO)(As ₃) ₂ L ₂]	1490m	1310m	1035m	770m	7.92	-	2.93	-

signal for methyl protons appears in the region δ 2.92-2.94 PPM. The resonances due to imino proton in the ligands observed at δ 1.51-1.52 PPM is absent in the spectra of complexes suggesting the formation of R_u-N bond and deprotonation of N-H group on complexation.

The ^{31}P NMR spectra of three complexes were recorded in order to confirm the presence of groups and to determine the stereochemistry of the complexes. The appearance of a signal around 28.82 PPM in the spectra of complexes confirmed the presence of magnetically equivalent phosphorous atoms and thus suggesting that

two groups are trans to each other in octahedral structure²⁴ (II).



(Oh, Str. of Ru (II) complexes)

($E = P/As$; $R = -C_4H_9$; $-CH_2C_6H_5$; $-2, 6 (CH_3)_2C_6H_3$)

REFERENCES

- Bennett M.A, Burce. M.I. and Matheson. T.W., comprehensive organometallic chemistry, vol. 4 edited by G. Wilkinson, P.G. A stone, E.W. Abel (Pergamon, Oxford) 796 (1982).
- Le Bozec H, Touchard D and Dixneuf P.H, *Advances in organometallic chemistry*, **29**: 163 (1989).
- Chung chen W, Lau C.P., Cheng S and Leung V.S., *J. organometal chem.* **464**: 103 (1994).
- Karidi K, Caroufic A, Tsipis A, Hadjiliadis N, Den Dulk. H, and Reedijk J, *J. Chem. Soc. Dalton Trans.*, 1176 (2005).
- Anderberg P.I., Harding M.M., Luck I.J., and Turner P. *Inorg. Chem.* **41**:1365 (2001).
- Balasubramanian K.P, Manivannan S, and Chinnusamy V. *J. ultra chem.* **4**: 15 (2008)
- John E.K and green M.A. *J. Med. Chem.* **33**: 1764 (1990)
- Santos L.G., Hagenbach A. and Abram U.J. *Chem. Soc. Dalton Trans*, 677 (2004)
- Mitchell C.L, *Toxicol Appl. Pharmacol.* **6**: 23 (1964)
- Kulyabko, P.N and Dybenko, R.G, Pel'kis, giya, **9**: 633 (1969)
- Tarakhovsk II, M.L et al., *Fiziol Aktiv. Veshchestva*, **3**: 119 (1971)
- Cowper, A.J., Astrik, R.R and Thakar, K.A., *J. Indian Chem. Soc.* **58**: 1087 (1981)
- Lieber, E, and Ramchandran, J., *Cana J. Chem.* **37**: 101 (1959).
- Ahmed, N; Levison, J.J; Robinson, S and Uttley, M.F, *Inorg. Synth.* **15**: 48 (1974)
- Sanchez Delgade, R.A; Lee, W.Y; Choi, S.R.; Cho; y; and Jun, M.Y., *Trans. Met. Chem* **16**: 241 (1991)
- Singh, T and Singh, J.P. *J. Indian Chem. Soc.* **69**: 241 (1991)
- Pandey R.N. and Sharma Richa, *J. ultra Chem.* **5(3)**: 361 (2009)
- Kaveri, M.V; Prabhakaran R; Karvembu R and Natarajan, K; *spectrochim Acta. Part A*; **61**: 2915 (2005)
- Pandey, R.N. and Singh Rajnish Kumar, *Oriental J. Chem* **25(3)**: 599 (2009)
- Pandey R.N, Anand A, Singh R.K and Kumar Amaresh *Asian J. Chem.* **22(7)**: 5601 (20 10)
- Singh B., Singh R; Choudhary R.V and Thakur K.P., *Indian J. Chem* **11**: 174 (1973)
- El-shahawi M.S and Shoair A.F., *Spectrochim. Acta. Part A*, **60**: 121 (2004)
- Kanchanadevi S, Balasubramanian K.P, Chinnusamy V, Karvembu R, and Natarajan K, *Trans. Met. Chem.* **30**: 330 (2005)
- Balasubramin KP, Raju V.V and Chinnusamy V., *J. Indian Chem. Soc.* **86**: 570 (2009).